

Review

Biomass Energy and Biofuels: Perspective, Potentials, and Challenges in the Energy Transition

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Abstract: Circular economy and sustainability are pivotal concepts in the discourse on the synergies between economic growth and environmental impact. As resource scarcity and environmental degradation intensify, advancements in energy conversion technologies become crucial for a sustainable economic model. Currently dependent on fossil fuels, the global economy must shift to a sustainable framework focused on bioenergy. Biomass, a renewable energy source, offers a promising solution by converting waste into valuable resources, reducing waste and environmental impact, and creating economic opportunities. Biofuels and bioproducts can meet energy needs while reducing greenhouse gas emissions and addressing global warming. Recent advances in biofuels, supported by initiatives and policies, promote more sustainable energy production. This paper aims to highlight the potential of biomass in meeting contemporary energy demand and provides an overview of biofuels and their production as a renewable alternative to fossil fuels. It also explores the future of agriculture and energy sectors, emphasizing global energy and environmental challenges and the competition between food and fuel feedstocks.

Keywords: biomass; renewable energy; biofuels; carbon neutrality; energy crops; waste-to-energy; biochemical processes; thermochemical processes



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1. Introduction

The socio-economic growth of any country is linked to its energy expenditure. Social development and human welfare depend on adequate supply, security, and efficient use of energy. For centuries, humanity has used fossil fuels derived from carbon sources that have contributed and continue to cause major climate and environmental imbalances [1]. Consumerism is the main cause of global change and the increase in the rate of natural resource extraction and the generation of huge amounts of waste, which, at the current rate of production and consumption, is expected to double by 2050 [2]. An alternative energy supply is the main step toward energy and environmental sustainability and will require the involvement of governments, businesses, institutions, and citizens themselves. This awareness is particularly present in the European context, given the EU's efforts to promote and implement the transition to an increasingly circular economy and to green, renewable, and sustainable energy resources. Indeed, Europe is facing a decisive energy turnaround that will bring an end to fossil fuel dependence and lead the continent toward climate neutrality, paving the way for a more sustainable future [3]. Nowadays, renewable energy is recognized as a vital element in mitigating climate change [4]. Renewable energy sources (RES) and the large-scale use of bioenergy are indeed attracting increasing interest in many nations and global areas. This is due to dwindling resources and rising prices of fossil fuels such as petroleum, coal, and natural gas. The growth rate for individual RES

in a given region of the world or country will depend on the geographical, climatic, and economic conditions [5]. In an effort to meet the world's demand for energy, reduce fossil fuel consumption, and cut CO₂ emissions, governments around the world are promoting the exploitation of renewable resources and energy such as biomass, wind, solar, and hydropower [1,6]. The potential of these renewable resources is considerable and can abundantly meet the world's energy needs [7]. Moreover, economic and social support for renewable energy systems is expanding rapidly. Confronted with the looming energy crisis, experts within the scientific community are intensively seeking long-term alternative solutions. Renewable sources such as solar, wind, geothermal, hydropower, and bioenergy derived from biomass are utilized for power generation, transportation, domestic use, and district heating, thereby enhancing energy security. Biomass is the most widespread form of renewable energy; it is believed to have growth potential due to its global availability. Biomass, known as a zero-carbon renewable electricity source, accounts for about 14% of total energy consumption and 38% of energy consumption in emerging countries [8]. The use of biomass feedstock for energy production reduces dependence on fossil fuels, thus contributing to the reduction in greenhouse gas emissions and the achievement of CO₂ emission reduction targets. Biomass is also a good substitute for fossil fuels from an environmental point of view. The use of biomass as an energy source can also foster the country's growth and the creation of economic and employment opportunities in the industrial and agricultural sectors. Biomass as an energy feedstock comes mainly from agriculture, forests, and various industries that process forest and agricultural materials, as well as from food waste and the waste disposal sector. In addition, it can be produced specifically through crops and cropping systems, traditional or innovative, whose purpose is energy. Soil is fundamental for the production of biomass for energy purposes, with particular attention to the sustainable use and protection of arable land [9]. Some materials can be used directly as fuels due to their properties, while other materials require pre-treatment with specific technologies before they can be used. Waste biomass is converted to energy by biochemical and thermochemical conversion methods [10]. When organic waste is decomposed by thermochemical or biochemical mechanisms, the chemical energy contained in the chemical bonds is transformed into thermal energy. Many studies have examined various approaches that combine thermochemical and biochemical conversion mechanisms to generate biofuels. Products such as bioethanol, biohydrogen, bio-oil, bio-char, biogas, and biomethane appear promising due to their bioconversion from waste materials [11]. In order to promote the use of increasingly advanced techniques and procedures that are effective in terms of energy, economic, and environmental sustainability, a thorough understanding of the biological and technical mechanisms that govern biomass production and transformation processes is essential. This research paper aims to present a general overview of potential biomass conversion methodologies and highlights the importance of their use in meeting current and future energy demand. The authors, with the aim of providing a clear information and awareness tool, analyzed the advantages and limits of the conversion of biomass and residues into solid, liquid, and gaseous biofuels. Biofuels were considered immediate and lasting solutions to reduce energy and mobility-related greenhouse gas emissions while providing environmental benefits. This paper also would like to suggest some important challenges that need to be addressed to maximize resource use and minimize environmental effects. The implementation of integrated biomass management strategies and processes and the development of efficient conversion techniques can ensure positive effects on both the environment and the economy. Research should be pursued to improve biofuel production by integrating circular economy concepts to ensure sustainability and achieve the set goals.

2. Methodology

To conduct the research for this review, Scopus and Google Scholar databases were utilized; the research timeline was conducted from 2020 to 2024. Keywords related to studies discussing the advantages and limitations of converting biomass and residues into

solid, liquid, and gaseous biofuels were selected. Therefore, keywords such as “Biomass, renewable energy, biofuels, carbon neutrality, energy crops, waste-to-energy, biochemical processes, thermochemical processes” were combined using Boolean operators “AND” and “OR”. The initial search yielded 331 studies; thus, the studies were screened by reading the title and abstract. The choice of articles was made only by considering English-language publications. Studies that did not meet the objectives of this review were excluded. Therefore, the remaining studies were screened by reading the full text. From this initial phase, 256 studies were considered. Subsequently, the remaining studies were analyzed by reading the full text. Consequently, 224 studies were selected for this review. Inclusion/exclusion criteria were carefully followed during the selection phase to ensure inclusion in the review of only those studies that were relevant and relevant to the authors on the theoretical basis of the totality of the selected keywords. The authors carefully evaluated each selected study to extract the relevant data and analyze them thoroughly to obtain valid, meaningful, and temporary conclusions about the subject matter.

3. Results

From the final analysis of the review of scientific articles selected for this paper, an estimation was made from the scientific point of view of the countries most interested in the topic. The number of scientific articles produced by a country or area is a useful indicator of the research activity of those entities. According to the authors, it is of considerable importance to examine the various trends and activities of nations or regions in relation to the research area under study. From our searches of scientific literature, it emerged that the countries that conducted more investigation and the countries most interested in the study of renewable resources are primarily India, China, the United Kingdom, and the United States of America (Figure 1). However, interest and investigation are widespread worldwide, with a greater interest from the Asian and European continents.

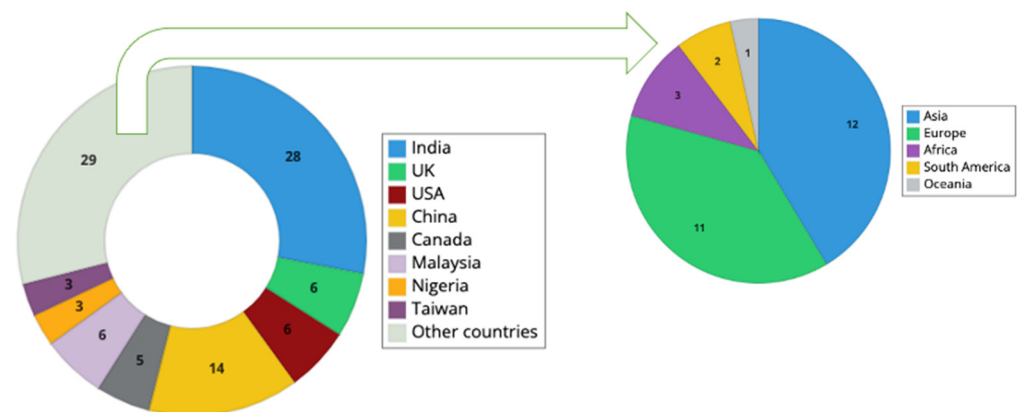


Figure 1. Geographical distribution of studies. Data are expressed as percentage (%).

3.1. Current Status of Renewable Energy Sources

Elements such as global warming, climate change, energy security, and reduction in greenhouse gas (GHG) emissions are driving the progress of renewable energy. Renewable energy is essential to promote environmental protection and sustainable development. Investment in renewable energy is also a new engine for economic growth, increased national income, growth in industrial activities, and direct and indirect increases in employment [12]. Bioenergy is a crucial component in promoting the sustainable development of nations, both contributing significantly to energy security and combating climate change. In this context, the transition from conventional fuels (i.e., coal, natural gas, and oil) to renewable energies (i.e., solar, wind, biomass, hydroelectric, and geothermal) poses several global challenges that require integrated and sustainable approaches. Renewable energy sources have many potentials and advantages and are increasingly used in different countries.

A list of available renewable energy resources, along with potential applications, is summarized in Table 1.

Table 1. Use of renewable resources [13–15].

Renewable Energy	Different Uses
Solar	Electrical, thermal or mechanical energy
Wind	Electricity generation
Biomass	Heat, electricity generation, synthesis of fuels and bioproducts
Geothermal	Power generation, heating buildings, hot water and agricultural drying
Hydroelectric	Power generation

Alternative and renewable energy sources such as hydropower, wind, solar, and biomass serve as economic and environmentally friendly substitutes to increase energy security [16]. The growth of solar energy technology has been exponential over the years. The use of solar thermal energy (conversion of light to heat) and solar photovoltaic energy (conversion of light to electricity) has found application in numerous sectors, such as residential, desalination, transportation, drying, and irrigation [17]. The former form of energy makes use of solar collectors, while solar photovoltaic energy uses photovoltaic solar cells. Research and development to optimize their design to increase the efficiency of solar energy collection is being studied by experts. The PVT (hybrid photovoltaic–thermal) innovation (a hybrid system combining both modes of solar energy harvesting) is able to utilize greater amounts of solar spectrum with higher temperature resistivity and higher efficiency [18]. This hybrid system maximizes energy production and makes maximum use of available solar resources, thereby reducing energy costs. Solar energy is reliable, affordable, sustainable, and renewable. In addition, it has a lower maintenance cost than other renewable energy sources and provides long-term service. However, the biggest drawback of solar energy is its intermittent nature, as it depends on the presence of the sun and varies with daily and seasonal weather conditions. This intermittency can make it difficult to ensure a constant supply of electricity, especially in situations of peak demand or scarcity of natural resources. Wind power, which uses wind speed to generate electricity with the help of a turbine, is also an intermittent and not constant source of energy, as it depends on weather conditions. On the other hand, wind power is among the most economically advantageous renewable energy sources and has the lowest benefit-cost ratio and large power generation capacity [19]. A totally weather-independent energy source is geothermal energy, which is energy that harnesses the heat in the planet’s crust and subsoil to produce electricity. It is, in fact, a clean source with a high availability factor and, above all, is reliable; it also has a higher efficiency than solar and wind power [20]. It can be used for power generation, building heating, hot water production, and irrigation in agriculture [21]. However, the total installed capacity of geothermal electricity is much lower than that of solar and wind power. According to the International Energy Agency (IEA) report, the global increase in renewable electricity in 2023 was mainly driven by the solar photovoltaic (+116%) and wind (+66%) markets, confirming China as the undisputed leader in these fields [22]. These markets will continue to grow in the coming years due to their lower generation costs compared to other alternatives, both fossil and non-fossil, also supported by ongoing policies by countries. The growth of the renewable energy market has also been spurred by the increased focus on environmental sustainability by many countries and companies, which are adopting policies and strategies to reduce greenhouse gas emissions and mitigate climate change. Hydropower is a significant source of renewable electricity, derived from water. It harnesses the kinetic energy of rapidly moving water as it descends from a high elevation, converting this energy into electricity by driving the blades of a generator turbine [23]. Its main advantages are its low operation and maintenance costs and considerable energy storage capacity to meet even periods of peak demand [19,24]. The most intriguing and promising renewable energy source

is biomass energy, a clean and renewable form of energy generated from organic matter, including plants and animals [25]. Biomass-based energy systems are distinguished by their ability to produce both heat and power, in addition to the wide availability of feedstock. Biomass has been widely used to obtain heat, energy, chemical feedstocks, and electricity using various conversion methods. Some of the most common biomass resources include wood, sawdust, straw, agricultural waste, food processing waste, forest residues, timber, crops, household waste, and wastewater [26]. Biomass, unlike other sustainable energy sources, can directly produce fuel along with chemicals [27]. Biofuels are considered a more flexible renewable energy source and can be easily stored and transported, allowing for more efficient distribution and greater energy independence. On the other hand, extracting energy from biomass could produce higher carbon emissions than fossil fuels and could also have consequences for biodiversity [23]. Among the developed renewable energy resources, bioenergy is considered one of the world's largest and most promising renewable energies and a nearly CO₂-neutral fuel [28]. To meet the energy needs of communities, recent studies have shown that the combination of multiple hybrid renewable energy systems is more cost-effective, stable, efficient, and reliable than a single energy system. It is well known that the intermittent nature of renewable energy sources remains a significant challenge in creating reliable and durable clean energy infrastructure [29]. Fluctuations in seasonal renewable resources lead to instability in renewable energy production during the months of the year. To address these issues and create an efficient power grid, the development of hybrid renewable energy systems (HRES) has been recognized as the best sustainable way to respond to global energy shortages. There have been developments of solar–biomass hybrid energy systems [30], solar–wind–biomass [31], and solar–wind–biomass fuel cells [32]. These examples are just some evidence of new scenarios combining renewable energy sources. Some authors have shown that wind, solar, hydro, and biomass energies, if integrated into the current energy system, can cover up to 40% of annual electricity demand while decreasing greenhouse gas emissions [33]. Another example is the rural electrification project described by Li J. et al. [34], using combinations of photovoltaic panels, wind turbines, and biogas generators, modeled and optimized to ensure reliable energy supply for residential, community, commercial, and agricultural demand in a given study area [34]. To successfully integrate sustainable energy sources into current energy systems, however, obstacles such as inadequate infrastructure, administrative-bureaucratic hurdles, and financial constraints must first be resolved [20].

3.2. Recovery of Products from Biomass

To meet the growing global energy demand and to achieve sustainable energy development goals, biomass plays a key role in the current and future energy landscape, while offering the greatest potential to meet the energy needs of modern society for both developed and emerging markets around the world [35,36]. Indeed, biomass represents a viable alternative to fossil fuels, as it is a non-fossil organic material that contains inherent chemical energy and can help reduce greenhouse gas emissions into the atmosphere. Its worldwide potential is estimated at 200–500 EJ of energy per year [37]. Biomass provides 14% of the energy used worldwide and is classified as a clean, renewable, continuous, and programmable energy source with significant growth prospects [38]. Its use for energy purposes is widespread and established globally. Biomass energy comes from sources such as agriculture, forestry, livestock, agribusiness, wood processing, and waste. Biomass materials used as renewable sources are summarized in Table 2.

Table 2. Common sources of biomass [8,39,40].

Biomass Sources	Products
• Agricultural waste	Sugarcane bagasse, rice husks, corn stalks, wheat straw, pulp, peel, stubble, cereals
• Municipal solid waste	Household waste, paper, food, garden waste
• Forest residues	Sawdust, wood waste and shavings, timber, leaves and bark, bamboo
• Livestock waste	Animal excrement, slurry, animal manure
• Sewage sludge	Sewage waste
• Agro-food waste	Pre-consumer food waste, production waste, post-consumer food waste (e.g., food, rice, vegetables, fruits)
• Industrial residues	Waste from the petrochemical, pharmaceutical, agricultural and food industries.
• Algal biomass	Microalgae and macroalgae

The use of biobased materials is considered a viable strategy for long-term energy supply and CO₂ emission reduction, as well as a strategy that offers benefits for the environment and rural economies, particularly in developing countries [41]. Different biomasses can be used to create environmentally sustainable fuels, materials, and chemicals through thermochemical and biological processes [42].

Figure 2 schematizes the concept of using various biomass sources, for sustainable and renewable energy purposes.

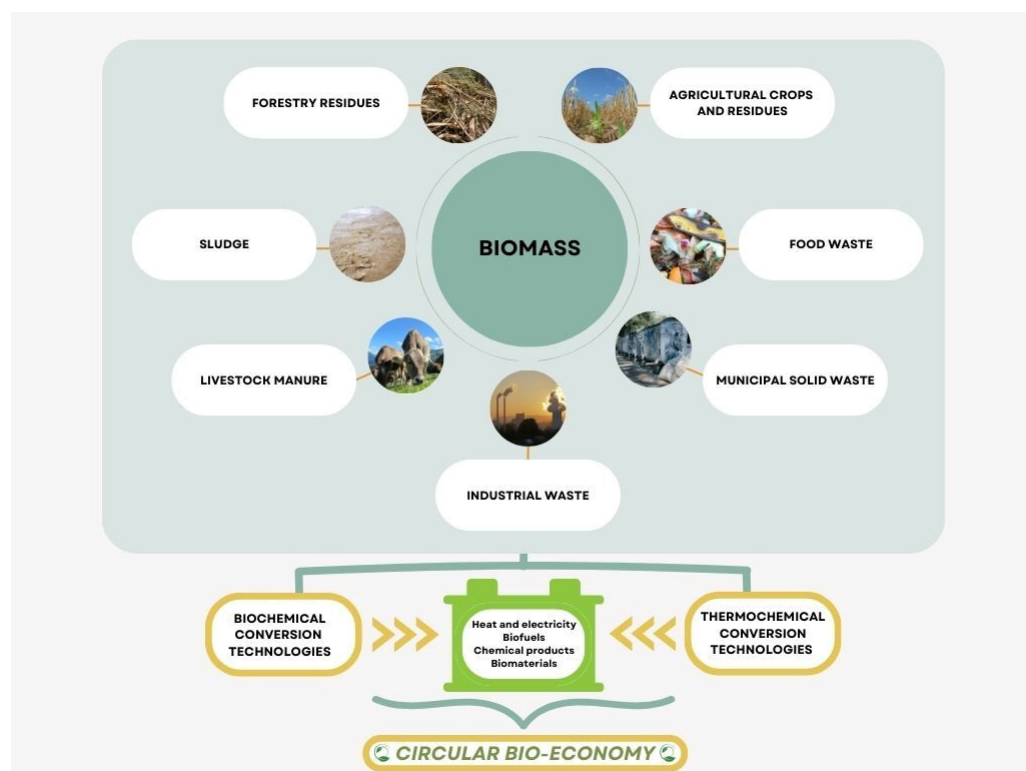


Figure 2. Integration of biomass utilization conversion technologies, in a bioenergy-based circular economy approach.

Biomass waste is very diverse in terms of chemical composition, so it is critical to select the best process for biomass valorization. There are numerous technologies for biomass valorization, such as direct combustion, biochemical technologies such as fermentation or anaerobic digestion, and thermochemical technologies such as torrefaction, pyrolysis, gasification, or hydrothermal liquefaction [43]. They will be discussed in detail below. The main advantage is that it is a predictable energy resource of a renewable nature that can be easily stored, transported, and used far from the point of origin [44]. However, there are also challenges in the production and use of biomass, such as high moisture and oxygen content, low calorific value, and highly variable properties. Other challenges include competition with food resources, competition for land use, production costs, and the need to develop efficient technologies for its conversion to energy [45]. Biomass resources can be classified into first-generation, second-generation, third-generation, and fourth-generation biomass, depending on whether they come from food crops, lignocellulosic biomass or microalgae, respectively [46]. The increasing need for biomass for bioenergy purposes intensifies the competition between traditional and emerging biomass uses. The next chapter will discuss and examine this issue. Feedstock availability, conversion efficiency, economic feasibility, and environmental impact are aspects to be considered in the processes of converting biomass into biofuels and bioproducts [47]. Emerging biofuels are generated from a variety of organic materials. Lignocellulosic biomass (LCB) is the most commonly generated waste from agricultural, agribusiness, forestry, and household production and is an abundant resource that can be harnessed for clean/green energy generation [48]. Wastes such as wood, paper, and cellulose; agricultural, forestry, and agro-industrial wastes; dedicated energy crops; and municipal solid waste are the main sources of lignocellulosic biomass [49]. In particular, rice straw, corn stover, wheat straw, sugarcane bagasse, and cotton stalk are the best lignocellulosic choices because they are renewable resources that are abundant, rapidly produced, and have a lower cost than other types of feedstocks. The origin of the types of biomasses, residues, or crops specifically grown for processing into solid, liquid, and gaseous biofuels is extremely diverse, as are the characteristics and qualities that characterize them and distinguish the final products. The most important biomass-based alternative biofuels can be classified into bioethanol, biodiesel, biogas, biomethane, biomethanol, and bio-oil [50]. Bioethanol produced from biological resources is considered an alternative, renewable, and sustainable energy source in the context of the circular economy [51]. It is the most widely used liquid fuel for transportation and is derived from the hydrolysis, fermentation, and distillation processes of sugar- and starch-containing crops and lignocellulosic materials. In addition to these conventional resources, bioethanol can also be obtained from algal biomass or through the use of engineered cyanobacteria [52]. Bioethanol is mainly used as an alternative to standard fuels, but it can also be integrated as an additive to gasoline without any modification to the engine [53]. Bioethanol consists of more oxygen, which allows for cleaner combustion in engines and reduced emission of pollutant gases into the environment [51]. In addition to its role as an alternative to fossil fuels, bioethanol serves as an important chemical platform for the production of ethylene, ethylene glycol, and their derived polymers, such as polyethylene and polyethylene terephthalate [54]. Biobutanol has also been the subject of interest as a substitute for conventional fuel because it is more compatible with combustion engines. Similarly, it can be mixed efficiently with gasoline and can be used in vehicles without the need for any modification in engine parts. Biobutanol has important superior properties, such as low volatility, high energy content, and a less corrosive and less hygroscopic nature than conventional fuel [55]. In addition, it can be used as a high-value chemical feedstock in numerous industrial uses, such as paints, cosmetics, adhesives, inks, food flavorings, solvents, surface coatings, materials, and in pharmacological fields [56]. It can be synthesized through the petrochemical route (more expensive) or by anaerobic fermentation (acetone–biobutanol–ethanol–ABE fermentation) of lignocellulosic biomass, using anaerobic bacteria, predominantly of the genus *Clostridium*. Biobutanol is a promising choice because of its potential as a quality sustainable fuel, as an efficient industrial solvent, and as a precursor in some important reactions [57].

Biodiesel commonly refers to the liquid fuel derived from vegetable oils, animal fats, and grease through different processes (transesterification reaction, thermal cracking/pyrolysis, microemulsification). It offers many advantages over petroleum-based diesel fuel due to its renewability, biodegradability, low emission profile, non-toxicity, and high flash point [58]. Biodiesel can be used at different concentrations, alone or blended with petroleum diesel, to create a biodiesel blend without the need for modifications in existing diesel engines. The cost of biodiesel is the main obstacle to commercializing the fuel, as it is linked to conventional feedstocks [59]. The use of edible feedstocks such as rapeseed, palm oil, corn, and sunflower has given way to the use of inedible oilseeds (Jatropha, Karanja, Mahua, castor bean, neem, rubber tree, tobacco seed, and rice bran) and the use of microalgae and cyanobacteria [60]. Non-edible oil seeds have potential related to their higher oil content and higher yield of glycerol compounds; however, the main challenge presented is their high free fatty acid (FFA) content. Biogas (a mixture of methane and carbon dioxide) is the by-product of microbial metabolism under anaerobic conditions, of the process known as anaerobic digestion (AD). Biogas can be used in its raw form primarily for heat and energy production and for the production of value-added chemicals for energy applications and industrial processes [61]. By consolidating and optimizing the anaerobic digestion process, biogas can be a continuous and stable source of energy. Recently, there has been a growing interest in the anaerobic digestion process aimed at producing biogas and purifying it into biomethane [62]. Biogas upgrading aims to increase the concentration of methane (CH_4) through its separation from other biogas compounds. Biomethane can be obtained through biogas upgrading separation technologies or by methanation of hydrogen and carbon dioxide [63]. Biomethane has comparable characteristics to natural gas, making it attractive for injection into the natural gas grid for a variety of end-use applications, as a heating fuel or for transportation in the marine and automotive sectors. Among the biofuels explored, biomethanol has shown promising potential for sustainable energy. Methanol is mainly produced from fossil fuels such as natural gas and coal; however, attention is shifting toward the sustainable use of biomass for biomethanol synthesis [64]. To obtain biomethanol, the starting biomass can undergo processes of gasification, pyrolysis, or can be subjected to microbial action through the AD process. Biomethanol is an important automotive fuel (both as a direct fuel and as a fuel blend), and it is also an essential feedstock in the chemical industry as it could be further used to synthesize formaldehyde, methyl tertiary butyl ether (MTBE), dimethyl ether (DME), or biodiesel [65]. Researchers are also actively working toward the efficient production of H_2 as a clean and sustainable energy source alternative to conventional hydrogen. Hydrogen is much more advantageous than any other fuel because it has the highest energy [66]. Biohydrogen, hydrogen produced through renewable energy sources, is suitable for gradually replacing fossil fuels. The production of biohydrogen is done through the use of biological processes such as biophotolysis of water by microalgae and dark fermentation and photofermentation of carbohydrate-rich organic matter (agricultural wastes, garbage, algal biomass, and the waste) by microorganisms [67]. The dark fermentation process has been found to be the most efficient in practical terms because it requires relatively low external energy input to drive the reaction, and the rate of hydrogen production is faster than biophotolysis and photofermentation [68]. It can further be generated by chemical processes that transform biomass into a high-hydrogen gas through thermochemical treatments (pyrolysis, liquefaction, and gasification), followed by hydrogen separation [69]. Biohydrogen is the most promising and ideal energy source for ensuring energy security and environmental sustainability due to its high calorific value and zero emissions in its production. However, research is still ongoing, and large-scale commercial production has not yet been achieved.

4. Biofuels: Alternative to Conventional Energy Sources

Biofuels are an increasingly viable substitute for fossil fuels on a global scale, emerging as the most promising sustainable energy source. In particular, bioethanol and biodiesel have attracted much interest because of their ability to integrate with conventional fuels

(gasoline and diesel) and their cleaner burning qualities [70]. Generally, biofuels are more sustainable than fossil fuels in terms of greenhouse gas emissions and environmental impact [71]. Biofuels may be produced from edible and non-edible raw materials. They derive from renewable resources such as agricultural waste, forestry waste, and municipal waste, used mainly as liquid transportation fuels [72]. According to their technology, processes, and raw materials used, biofuels are divided into four types: first, second, third, and fourth generation [73]. Figure 3 shows the raw materials used in the production of biofuels.

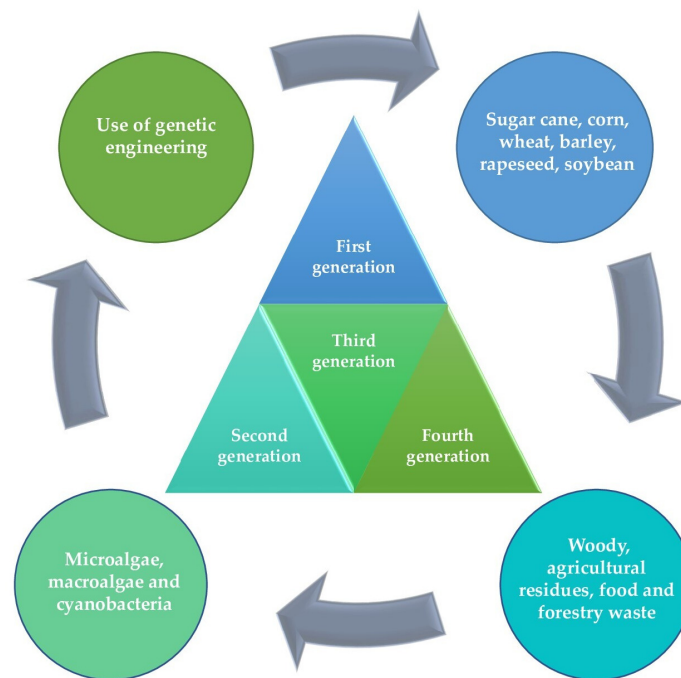


Figure 3. Variety natural resources used for the production of biofuels of several generations. Please note that the colors in the figure correspond to the raw materials used for each type of biofuels produced.

The production of biofuels from various biological sources through the use of various emerging technologies and biological processes is clearly growing on a global scale [72]. The wide range of production opportunities and the potential for innovation in the biofuel sector meet the requirements for the development of sustainable technologies that contribute to the reduction in greenhouse gas emissions.

4.1. First Generation Biofuels

First-generation biofuels are produced from a wide range of agricultural energy crops, as shown in Table 3. First-generation biofuels are mainly divided into bioethanol and biodiesel.

Table 3. Feedstocks for biodiesel and bioethanol production [11].

Different Agricultural Energy Crops	Products Used
Sugar-based crops	Sugarcane, sugar beet, sorghum
Starch-based crops	Corn, barley, wheat
Oil-based crops	Rapeseed, sunflower, palm

Energy sources derived from sugar (i.e., sugarcane, sugar beet, sorghum), starch (i.e., corn, barley, wheat), or oil-based crops (i.e., rapeseed, sunflower, palm) are included in this group of fuels [11]. Popular agricultural crops for generating these biofuels include corn (*Zea mays* L.), wheat (*Triticum aestivum* L.), sugar beet (*Betavulgaris* L.), cassava (*Manihot esculenta*), rapeseed (*Brassica napus* L.), and sugarcane (*Saccharum icinarum*) [74]. Biodiesel is produced through the process of transesterification to extract the oil from oil plants and convert the vegetable oil into fuel that can be used directly by engines. Transesterification involves the chemical reaction between lipids and alcohols, usually methanol or ethanol, to form methyl or ethyl esters in the presence of a catalyst, such as sodium or potassium [58]. The product of the process is a more sustainable fuel than conventional diesel, as it produces fewer harmful emissions and contributes to the reduction in environmental impact. In addition, the production of glycerol as a high-value co-product offers additional benefits, as it can be used in the chemical and cosmetic industries. Biodiesel is mainly obtained from rapeseed, soybean, or palm oil from Europe, South America, and Asia, respectively [75]. In general, tropical and subtropical countries have strong potential in biofuel production due to their favorable climatic conditions for growing feedstock. Further, they also have greater availability of agricultural land and natural resources that can be used for this purpose. Starch-based components such as potatoes, barley, corn, cassava, and wheat are used for bioethanol, as are sucrose-containing plants such as sugar beet, sweet sorghum, and sugar cane. The simple fermentation process of sugar extracted from such crops, with subsequent distillation, is adopted for bioethanol production. Variations of the fermentation process refer to different temperature and pressure conditions, depending on whether the type of feedstock used is starch based or sugar based [76]. Bioethanol is the most widely used liquid biofuel in the transportation sector, with the United States and Brazil as the main producers [77]. Despite the successes achieved in the production and commercialization of first-generation biofuels, they have raised a number of questions and concerns about food supply, food security, and arable land requirements [11]. Their production causes direct competition between agricultural resources used for food production and those used to produce the fuel itself, thus leading to a reduction in the area available to grow food and an increase in its cost. The cultivation of energy crops wastes water, energy, and land resources that are critical for food agriculture. Future sustainable biofuel production allows the identification and use of resources that do not pose a conflict between food and fuel supply, ensuring sufficient arable land for food and also considering population growth [78].

4.2. Second Generation Biofuels

In response to the controversy surrounding first-generation biofuels, numerous efforts have been made to utilize inedible feedstocks for biofuel production [79]. For this purpose, feedstocks that neither compete with food agriculture nor require cultivation are used, as they are derived from waste biomass. This approach offers significant advantages in terms of environmental and social sustainability. Second-generation biofuels use lignocellulosic biomass from agricultural and forestry residues as well as food industry waste. This feedstock is quite cheap, readily available and available in large quantities [80]. Plant biomass utilizes sources such as agricultural, woody, and forestry wastes and the green waste derived from gardens and parks [81]. Some examples include straw, straws, chaff, wood chips, sawdust, tree prunings, grass clippings, leaves, stumps, and twigs. Lignocellulosic biomass consists mainly of cellulose, hemicellulose, and lignin, which must be converted into fermentable sugars before they can be converted into biofuels. Lignin makes it difficult to naturally unlock fermentable sugars by hydrolysis, reducing the efficiency of fermentation [76]. This requires the application of effective pretreatment methods. The main objective of pretreatments is to remove lignin without compromising the main structure of cellulose [80]. The adoption of these practices is essential to achieve high yields and improve the stability of biofuels, although they result in increased cost and time in the production process. More research is aimed precisely at reducing the overall production cost, which requires improved and advanced techniques for converting

cellulosic and hemicellulosic biomass to sugars, low pretreatment energy consumption, and more efficient separation technologies [82].

4.3. Third Generation Biofuels

Microalgae, macroalgae, and cyanobacteria are the main photoautotrophic microorganisms used as biomass feedstock in third-generation biofuels [83]. Most algae grow as photoautotrophs, through oxygenic photosynthesis. Algal biomass has been widely considered and studied for its high lipid productivity. Microalgae have, in fact, a very high growth rate. According to Shokravi et al. [84], microalgae show higher rates of photosynthesis than terrestrial plants and grow rapidly, producing 20–300 times more oil than conventional biomass crops. The main advantage of using microalgae as a raw material is the low cost of cultivation because microalgae can grow in a marginal wetland area or in wastewater. They are also considered advantageous resources because of their ability to survive in adverse conditions. Indeed, lipid production is optimal when microalgae are grown under certain abiotic stress conditions (e.g., nitrogen, light, temperature) [85]. The conversion of lipids to biofuels occurs through transesterification, while other elements such as starch, cellulose, and carbohydrates are converted by hydrolysis processes [79]. The absence of lignin and low levels of hemicellulose in algal cell walls promote increased hydrolysis and fermentation yields [86]. Other important characteristics of algal biomass include reduced need for space to grow, high oil content, better environmental adaptability, a shorter growth cycle, and higher photosynthetic efficiency [87]. Microalgae are the intensified resources of third-generation biodiesel production and are therefore considered a very promising renewable energy source.

4.4. Fourth Generation Biofuels

Fourth-generation biofuels include the use of genetic engineering to increase the desired characteristics of organisms used in biofuel production [88]. The use of this approach allows increasing the value of product diversity, yield, concentration, and productivity of organisms for improved fuel production. In recent years, there has been an increase in the implementation of strategies for the use of advanced biotechnological techniques to enhance the productivity of biosynthetic pathways present in organisms by eliminating competing pathways [89,90]. The organisms being used refer to microalgae, yeasts, fungi, and cyanobacteria. Various genetic modification approaches have been undertaken to improve the yield and economic efficiency of bioenergy crops. These apply to a range of characteristics, such as the use of more types of sugars (e.g., pentoses and hexoses), increased lipid synthesis, or increased photosynthesis and carbon fixation [91]. The metabolic versatility of microorganisms allows the use of various substrates to produce a wide range of biofuels, such as ethanol or other fuel products such as butanol, isobutanol, and modified fatty acids. Efficient production of fourth-generation biofuels as a robust future solution to the emerging demand for alternatives to fossil fuels can only be achieved through the use of synthetic biology. Fourth-generation biofuels represent significant progress compared to previous generations as, through genetic manipulation of the strains of interest, clean and sustainable forms of energy are obtained that effectively meet technical and economic requirements [78,79]. It is possible to refine biofuel production through the development of new strains and the integration of different genetic engineering approaches [92].

4.5. Impact and Prospects of Biofuels

The use of biofuels has increased significantly over the past decade, with the United States and Brazil leading the way as the largest domestic producers [93]. Quantitative data about production from 2020 to 2023 are shown in Figure 4.

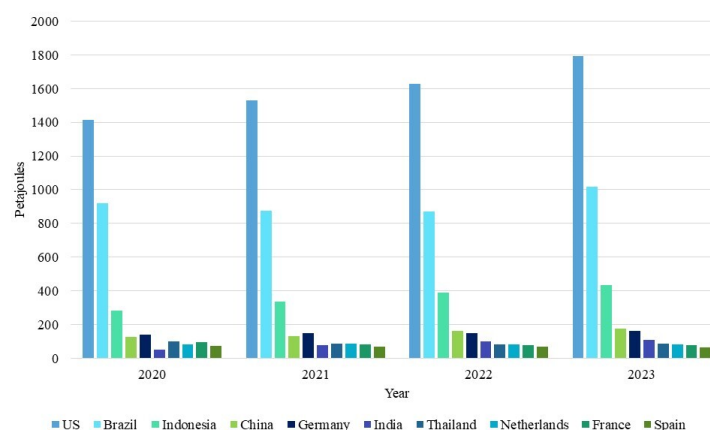


Figure 4. Top ten producer countries of biofuels. Data refer to bioethanol and biodiesel production [94].

The biofuels industry continues to evolve and expand globally, providing sustainable solutions to current environmental and energy challenges. Despite significant advancements, numerous challenges persist. Each generation of biofuels presents its own set of advantages and obstacles that must be evaluated within the context of the global energy transition. A key challenge in biofuel production and its sustainability lies in the competition between using land to grow biomass and ensuring food security [78]. To meet the growing need for agricultural raw materials, there is the potential risk of further deforestation and land use, especially in areas of high biodiversity. Indeed, one must consider the indirect change in land use. The cultivation of raw materials to produce biofuels, such as sugarcane, corn, wheat, and soybeans, competes with food production, and this becomes a problem when food resources are not enough for everyone [95]. Indeed, the use of food crops has generated food safety debates over the years, fueling the “food vs. fuel” controversy. This inevitably leads to an increase in the demand for edible commodities, with the direct consequence of increasing their prices. This situation has prompted researchers to look for non-edible alternatives as feedstocks in order to obtain cost-effective biofuels with comparative characteristics to conventional fuel [96,97]. Lignocellulosic biomass is considered a potential resource in this regard. However, lignin is an obstacle in the production process, as it resists the interaction of enzymes with the cellulosic structure during the hydrolysis step [98]. One challenge in the production of second-generation biofuels is to optimize the production process, both energetically and environmentally [99]. In addition to exploiting new raw materials of non-food origin, the areas devoted to such crops are also shifting to uncultivated lands (dry forests, ponds, swamps) in order to maximize the value of land use [100]. For example, the need for agricultural land is less for the cultivation of algal biomass and does not require complex procedures for its cultivation [101]. Microalgae provide an alternative and sustainable solution for reducing CO₂ emissions. In fact, microalgae fix CO₂ in the atmosphere, and biomass can be efficient in biofixing waste CO₂, playing a crucial role in reducing global warming and the greenhouse effect [102]. Further progress has been achieved through the recent development of synthetic biology. However, such production has low productivity, high production costs, and limited scalability [103]. That said, third- and fourth-generation biofuels appear promising and are considered the optimal solution to achieve sustainable development goals, but challenges considered must first be overcome. They are considered excessively expensive and lack competition in the fuel market. Further research is needed to delve deeper into third- and fourth-generation resources and their competitiveness. In any case, it is possible to overcome these barriers through the use of innovative, state-of-the-art strategies [104]. In addition, it is important to focus on optimizing their qualities, improving current processes, and implementing new methods of synthesis. Transportation and storage of biofuels are also critical aspects of ensuring the efficiency and sustainability of these renewable resources. Lack of adequate

transportation and storage infrastructure may limit the accessibility of biofuels. Biofuels have several characteristics that affect transportation choices and equipment design, such as flammability, density, viscosity, volatility, and corrosivity. Therefore, the transportation (road, rail, sea, pipeline network) and storage costs can be higher than those of fossil fuels, requiring significant investment. Steps have been taken in modifying current infrastructure to facilitate biofuel transportation. This includes improving distribution and storage networks, as well as integrating biofuels into existing pipelines.

5. Biofuel Production Processes

Biomass can be converted into clean energy and value-added chemicals through different processes. Direct combustion is the most common process for obtaining heat and energy from waste biomass, which is used to provide heat and/or steam for cooking, space heating, and industrial processes, as well as for electricity generation [105]. However, this approach has low energy efficiency and can lead to global warming due to harmful emissions of large amounts of carbon dioxide into the environment [106]. Therefore, researchers' attention has focused on two main routes of converting biomass into valuable forms of bioenergy: the thermochemical process and the biochemical process. The identification of the best methods of biomass valorization depends on several factors, such as the type and characteristics of biomass, its location, quantity, environmental regulations, economic considerations, and desired end products (solid, liquid, or gaseous) [107]. The main technologies and their products are shown in Figure 5 and discussed below.

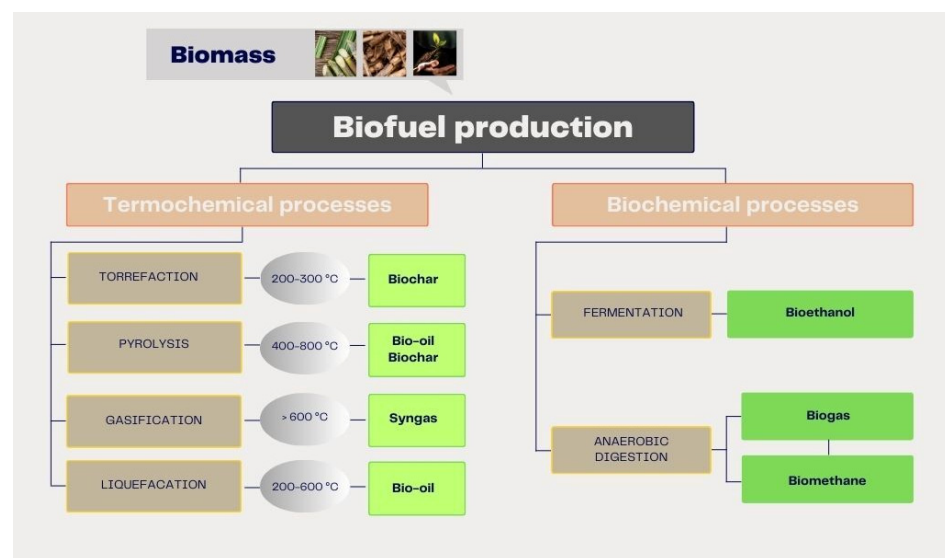


Figure 5. General outline of thermochemical and biochemical conversion to produce biofuels.

5.1. Thermochemical Conversion Processes

Thermochemical conversion pathways are among the most widely applied techniques in the conversion of biomass to produce solid, liquid, and gaseous biofuels. They use the combination of heat and chemical reactions to convert organic biomass into fuels and green chemicals. Thermochemical conversion has emerged as the most promising mode of utilization, attributed to its inherent characteristics of cost-effectiveness, rapid kinetics, and high-quality results [108]. The main thermochemical techniques include torrefaction, pyrolysis, gasification, and hydrothermal liquefaction [109–111], which will be discussed as follows.

5.1.1. Torrefaction

The biomass torrefaction process is generally carried out in the temperature range of 200 to 300 °C at slow heating rates, i.e., $<50 \text{ °C min}^{-1}$ in an oxygen-free environment [112].

Torrefaction is also often referred to as mild pyrolysis and has become a promising pretreatment technology to improve biomass for solid fuel production and to offset greenhouse gas emissions. Compared to pyrolysis, this process requires less energy input due to the use of lower temperatures [113]. The main product of torrefaction is biochar, which has properties intermediate between precursor biomass and charcoal [114]. In addition to the solid biomass, the volatile fraction represented by noncondensable gases (mainly CO₂ and CO, and in low concentrations also CH₄ and H₂) and some condensable gases or liquids (water, furfural, furans, phenols, and organics such as acetic acid, propionic acid, and formic acid) is also released [115]. The yield of the volatile fraction increases with the degree of torrefaction. The intended use for torrefied biomass is as a solid fuel in power generation, whereas the volatile fraction will be used to meet thermal energy needs through combustion. Torrefaction leads to several improvements in the characteristics of the torrefied product; this process makes it suitable for various applications such as combustion, co-firing, adsorbents, and soil amendment [116]. In fact, this process increases the energy density and hydrophobicity of the biomass and reduces its grinding energy requirement, making it less durable, more brittle, and with greater potential for subsequent applications [117]. In particular, its use as feedstock is more suitable for gasification, combustion, co-firing, and pyrolysis, significantly improving the energy density and heating value of fuels, as well as the quality of syngas and bio-oil produced. The heating value of biomass can reach up to 14–30 MJ kg⁻¹, which is almost comparable to that of coal-based fuel (about 25–35 MJ kg⁻¹) [118]. Torrefaction process parameters such as temperature, residence time, heating rate, biomass moisture content, and particle size play a role of direct influence on the final properties of torrefied biomass [119]. In addition, torrefaction reduces transportation costs and improves storage facilities by removing moisture from biomass. The water and ash content of biomass reduce energy yield, so decreasing or eliminating these components will increase the energy content of biomass [120]. For optimal torrefaction, the moisture content in raw biomass should not exceed 10%, but as this threshold is exceeded, it is necessary to undergo a drying process [121]. Torrefied biomass has lower atomic O/C and H/C ratios due to pretreatment, which makes the torrefied product similar to coal [122]. All these improvements provide the ability to process torrefied biomass on existing coal infrastructure without the need for significant additional investment [123]. The ideal feedstock for the torrefaction process is lignocellulosic biomass such as wood, energy crops, forest, and agricultural residues. During torrefaction, biomass polymers undergo physicochemical changes. Starting from 200 °C, significant decomposition of hemicellulose is observed; however, the physicochemical characteristics of biomass change more significantly with the degradation of part of lignin and cellulose at higher temperatures from 250–300 °C [124]. Roasting studies have largely been conducted on bamboo, beech, birch, eucalyptus, larch, pine, oak, willow, miscanthus, and scagliola, but roasting of various agricultural residues, such as almond shells, has also been examined, as have areca nut husks, coffee residues, corn cobs, cotton stalk, rapeseed stalk, rice husk, rice straw, wheat straw, sugarcane bagasse, olive waste, and oil palm waste [122]. Biomass can also be enhanced through wet torrefaction by adding water and dilute acid solutions at temperatures of 180–260 °C. In terms of energy consumption, wet torrefaction does not require pre-drying, so it results in greater energy savings than dry torrefaction. Recently, research has focused on new uses of torrefaction by-products, including torrefaction condensate as feedstock for biogas production and adhesive for plywood panels, and bioethanol production from torrefied biomass [125]. In addition, combining torrefaction with other pretreatment methods such as densification (briquetting or pelletization) could provide similar benefits to non-densified torrefaction, helping to reduce handling and transportation costs [126]. The application of torrefied products has opened up new opportunities in the renewable energy sector, significantly promoting the use of torrefaction in the energy supply chain [127].

5.1.2. Pyrolysis

Pyrolysis is an irreversible thermochemical process that involves the decomposition of organic matter from the starting biomass, resulting in the production of energy-dense products such as bio-oil, bio-char, and pyrolysis gas [94,128]. The process is distinguished by its ability to thermally decompose feedstocks in the absence of oxygen, or with less than the amount required for complete combustion [129]. Several reactions occur in parallel and in series during the lignocellulosic biomass decomposition process, such as dehydration, depolymerization, isomerization, aromatization, decarboxylation, and carbonization. The first reaction is the decomposition of hemicellulose, which occurs mainly between 250 and 350 °C, followed by cellulose, which decomposes at a temperature range of 325–400 °C, while lignin (the most stable component) is decomposed at a higher temperature range from 300 to 550 °C [130]. Depending on the operating conditions used in the process, the pyrolysis process can be divided into slow pyrolysis, fast pyrolysis, and flash pyrolysis. They differ from each other in temperature, solids residence time, heating rate, biomass particle size, and yield obtained [131]. Slow pyrolysis is characterized by relatively low temperatures (<500 °C) and long residence times; fast pyrolysis occurs at reaction temperatures from ~500–900 °C, with a higher heating rate and moderate residence times; and flash pyrolysis is characterized by very high temperatures (~900–1300 °C) and extremely short residence times [132,133]. These operating parameters are crucial in defining the composition, yield, and quality of the final products in the pyrolysis process [134]. Fast and flash pyrolysis are generally preferred for the production of high-quality bio-oils with higher yields, while slow pyrolysis is more suitable for coal production. The specific composition of the biomass used as feedstock also influences the performance of the pyrolysis process and the characteristics of the products formed [135]. Polymers such as cellulose and hemicellulose contribute to the formation of bio-oil, while lignin is more responsible for the formation of bio-char [136]. In terms of product yield, flash pyrolysis is more efficient for bio-oil production, while slow pyrolysis is more advantageous for bio-char and biogas production. Precisely, with the use of non-catalytic fast pyrolysis, using 25 kg h⁻¹ as biomass feeding rate, the bio-oil production yielded is 65.8 wt%, whereas bio-char is 15.4 wt%. The application of slow pyrolysis yielded the production of bio-char up to 79.16 wt% [137]. The bio-oil obtained from the process is a dark-brown liquid mixture containing many oxygenated hydrocarbons and is used for power and heat production and, if properly upgraded, can be used for transportation [138]. It also represents a resource of chemical compounds, which, once isolated and characterized, can be used in the chemical and pharmaceutical industries. Higher heating value of about 20 MJ kg⁻¹ and high energy density are the general characteristics of bio-oil [139]. Bio-char is a porous, carbon-rich organic solid residue. It is generally used as a solid fuel and soil conditioner in agriculture, while pyrolytic gas can be used as a gaseous fuel for thermal applications [140]. In addition, biochar is used in several other applications for its co-benefits, such as soil carbon sequestration, pollutant adsorption, soil water retention, pollution remediation, and carbon-based products [141]. Pyrolysis is increasingly relevant in today's energy sector and industries because of the variety of high-value products obtained through the process. It is also an advantageous process because the products obtained, mainly coal and liquid fuels, are easy to store and transport [142]. In addition, the pyrolysis process can be easily integrated with other biomass upgrading processes, such as anaerobic digestion, to increase the overall biomass conversion efficiency, minimize the overall process cost, and make the whole process more energy sustainable [143]. Although they are still under development and require further investigation, technologies such as microwave-assisted and solar-assisted pyrolysis have also attracted interest in recent times because of their higher energy efficiency compared with conventional pyrolysis [42,144]. New advances also involve the co-pyrolysis of biomass with other feedstocks. Some authors have shown that mixing two or more feedstocks other than biomass has improved the quality and quantity of pyrolysis products [145–149]. This optional technique shows promise for future applications in industry.

5.1.3. Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) is a thermal process that uses hot water compressed in a liquid or supercritical state at temperatures between 200 and 400 °C and higher pressures (10–25 MPa) to convert biomass into liquid fuel biocracking [150]. Biogrease/bio-oil is the renewable equivalent of petroleum, as it is a high energy density intermediate that can be upgraded to a variety of liquid fuels. The main advantage of the HTL process is the ability to directly process wet biomass, enabling the conversion of materials such as algae or slurry into bio-oil. The process saves a significant amount of energy as no dehydration/drying of feedstock is required, thus reducing costs and allowing the process to be conducted at relatively low temperatures [151,152]. Reportedly, bio-oil obtained from liquefaction has better fuel quality than pyrolytic oil due to its reduced oxygen content, which increases its stability and facilitates its use as a fuel [37,153]. However, the HTL process is not as attractive in the eyes of researchers compared to the pyrolysis process, as it produces a lower yield of bio-oil (between 20 and 55% by weight) and has a reduced heating value, requiring an additional catalyst or other reagents to facilitate the process [154]. Bio-oil yield is influenced by several process parameters. It has been observed that bio-oil yield typically increases with increasing temperature and reaction time and increases with a low water-to-biomass ratio, although for each parameter there is an optimum value above which yield decreases [155]. It has been, in fact, reported that a temperature for HTL at 350 °C, compared to 280 °C and 320 °C, allowed to yield higher levels of bio-oil. However, it is important to underline that the temperatures for yielding the highest-level bio-oil are strongly related to the type of feeding [155]. Bio-oil can be used in furnaces, turbines, engines, burners, and boilers and can be converted into a variety of alternative transportation fuels after proper upgrading, including automotive biofuels (biodiesel), biofuel, and aircraft biofuel [156]. Several strategies are being explored for bio-oil upgrading, including catalytic cracking, solvent addition, and hydrogenation that will improve the properties of bio-oil, making it more suitable for various industrial applications. Water is the most commonly used solvent in the liquefaction process, but other options may include organic solvents (dichloromethane, trichloromethane, and acetone) or a combination of both. The synergistic effect between co-solvents can significantly increase the yield of bio-oil, making it an optimal choice as a solvent in the liquefaction process [157]. In addition, research conducted in recent years has focused on bio-oil derived from hydrothermal co-liquefaction (co-HTL) of different biomass combinations. This approach makes it possible to improve the degree of liquefaction of each feedstock, the quality and yield of bio-oil, and to significantly reduce the logistical costs associated with biomass collection and transportation [152]. Due to the synergistic effect in biomass mixing, the overall efficiency of the conversion process can be improved. In addition, the flexibility of the process in using two or more biomasses makes it possible to cover variations in biomass maturation, both in terms of quantity and quality [158]. The co-processing of lignocellulosic biomass, microalgae, food processing residues, and sewage sludge has been the subject of numerous studies, and the authors have demonstrated beneficial synergistic effects on improving the energy recovery of bio-raw and its qualities [159–163]. These results are encouraging and promising, however, the desired synergistic effects are not always obtained, so a thorough selection of appropriate biomass feedstocks for co-HTL is necessary. Comparison of different feedstocks and their mixtures under the same conditions can further the understanding of the influence of compositions on the distribution of HTL products and further explore the synergism between different components [164]. In order to optimize the evolution and practical use of the mentioned processes, as well as to maximize the qualities of bio-oil and ensure its commercial viability, additional research should be conducted.

5.1.4. Gasification

Gasification is a process in which biomass is subjected to extreme temperatures, generally at a temperature above 700 °C, in the presence of a controlled oxidizing agent, resulting

in the production of synthesis gas (syngas), which contains mainly CO, H₂, CO₂, and CH₄ and a solid residue by-product consisting of ash and char [165,166]. In general, air, oxygen, steam, or their mixtures can be used as gasifying agents of the process, and the choice of gasification agent leads to a different composition of the gas produced. Gasification has emerged as an attractive, versatile, and highly efficient thermochemical process with advantages such as reduced NO_x and SO_x emissions, lower reaction temperatures, and lower oxygen demand [106]. It depends on a sequence of fundamental reactions such as drying, combustion, pyrolysis/devolatilization, and reduction, which must occur under optimal conditions to ensure the quality of the desired end product [167]. Gasification often involves multiple simultaneous processes, with exothermic reactions providing heat to endothermic ones as needed [168]. Initially, the moisture content of the biomass (30–60%) is vaporized or evaporated to values below 15%. Next, decomposition of the biomass into volatiles and solid residues takes place, which will interact with the gasifying agents, generating CO, CO₂, and H₂O. The process generates heat that reaches temperatures above 700–800 °C, leading to the formation of ash as the final residue [168]. The effectiveness of the gasification process can be influenced by the type of gasifier, biomass composition, and biomass size. In addition, each reaction is strongly influenced by fuel characteristics and process variables such as gasifying agent, gasification temperature and pressure, heating rate and residence time, biomass feedstock, and its grain size, all of which are key criteria for the selection, design, and operation of a given gasification system [169]. There are a large number of gasifiers: fixed-bed (updraft and downdraft), fluidized-bed (whirlpool, circulating, dual-, and multistage), and entrained-flow, which are the most common, followed by sprayed-bed gasifiers or plasma reactors. The syngas obtained can be used as an energy carrier for biofuels, hydrogen gas, biomethane gas, heat, power supply, and chemical feedstock supply [151]. Through the Fischer–Tropsch process, the produced gases can be further converted to liquid fuels through or can be converted to heat and power for combined heat and power (CHP) applications [170]. Syngas is also a key intermediate in the chemical industry. Indeed, it can be efficiently converted into other chemicals, including methanol and dimethylether (DME) [171]. Particularly, the conversion of synthesis gas to Fischer–Tropsch synthesis products is receiving significant attention due to its promising characteristics. Fischer–Tropsch synthesis is defined as a technology that converts biomass to a high-quality transportation fuel [172]. It is a catalyzed polymerization process occurring on the surface of a heterogeneous catalyst, where hydrocarbon monomers generated by the hydrogenation of adsorbed CO produce both short- and long-chain hydrocarbons. This process has a wide range of applications. From the perspective of the characteristics of the produced biofuel, the Fischer–Tropsch biofuel is comparable to other biofuels. However, in terms of sustainability, the Fischer–Tropsch process results in an advanced biofuel. The most remarkable aspect of the products obtained through Fischer–Tropsch synthesis is the absence of salts, heavy metals, sulfur, nitrogen, or aromatic compounds in the final products.

The gasification process is an excellent means of producing green hydrogen (hydrogen produced from renewable electricity by electrolysis), as it provides high overall system efficiency, a rapid process, and more choices for integration with other power generation systems [169]. Following the previous considerations, hydrogen has attracted increasing interest due to its high energy density and clean combustion properties. It is a relevant component of synthesis gas, not only as a promising energy carrier for replacing traditional fuels but also as a key chemical in the chemical industry for hydrogenation and hydrotreatment to synthesize products such as methanol, ammonia, and ethylene glycol [173,174]. It is important to perform detailed research to identify the appropriate gasifying agent to increase the percentage of CO₂ or H₂ depending on the application, considering the multiple advantages of CO₂ gas in the refrigeration and air conditioning industry, as well as hydrogen gas in fuel cells. Steam has been shown to be more effective than air in maximizing hydrogen yield [175]. The gasification process also generates unwanted impurities (tar, particles, nitrogen compounds, sulfur, chlorine, alkali, polycyclic aromatic

hydrocarbons, and heavy metals), so it is necessary to purify the synthesis gas before subsequent applications [176]. Gasification can be performed in different types of reactors, such as fixed-bed, fluidized-bed, entrained-flow, and plasma reactors, depending on the characteristics of the biomass feedstock, operating conditions such as temperature, pressure, and residence time, and the desired synthesis gas quality [177]. Feedstocks that can be used for biomass gasification include agricultural straw, different agricultural wastes, dry lignocellulosic energy crops, wood waste, livestock waste, municipal money waste, and other combustible materials. Feedstock pretreatment (drying, torrefaction, particle size reduction, fractionation and leaching, and densification) is a key step in the biomass gasification process, as it reduces moisture content, facilitates transportation and handling, and improves heating rate, uniformity, density, and fuel quality. The chemical and elemental composition of biomass, inherent mineral content, volatile content, moisture content, and physical qualities are all key elements in the gasification process, as they represent factors that influence syngas yield and composition [178]. As highlighted earlier, the use of torrefied biomass, due to its high heating value, increases the thermal performance of gasification systems. The use of biomass with lower moisture content promotes greater process efficiency, as it minimizes the energy requirement for drying and increases the overall energy yield [139]. When the carbon and oxygen content in the feedstock increases, there is an increase in the amount of carbon monoxide (CO) in the synthesis gas [179]. In addition, the size of the biomass particles also affects the gasification process. Smaller particles offer a larger specific surface area for gasification reactions, resulting in higher gas production and lower energy consumption, as well as higher efficiency in heat transfer and reaction rate [180]. Gasification-based bioenergy generation has been widely studied; however, it is still facing challenges related to limited energy efficiency, especially in small-scale development. Biomass gasification is a promising technology for obtaining value-added H₂-rich gases [181]. From this point of view, it is particularly important because the demand for hydrogen is constantly increasing. In fact, by 2070, global demand for hydrogen could exceed 500 million tons, and some estimates indicate that it could reach as high as 800 million tons/year [181]. However, despite the many advantages, there are still some challenges regarding biomass gasification, such as tar formation, low efficiency, process instability, and synthesis gas upgrading. For these reasons, active research works are currently underway in this area. Tar formed from biomass gasification is a complex mixture of high-molecular-weight aromatic hydrocarbons that can cause fouling, corrosion, and equipment blockage and is recognized as an undesirable product because it could block the gasifier, deteriorate the quality of the output gas, and cause environmental problems [182]. Tar is a major challenge in gasification that affects the quality and efficiency of syngas production. An optimized reactor, selection of the gasification agent, and use of a highly active and stable catalyst could reduce the gasification temperature, reduce particulate matter and tar, and improve the quality of the produced gas [183]. Ni-based catalysts, noble metal-based catalysts, natural catalysts, and coal catalysts have been shown to have high activity for tar removal [181]. In addition, various techniques, such as filtration, adsorption, and condensation, can be used to remove tars from the gas stream downstream of the gasifier [184]. Thus, there is a vast field of study related to all the above parameters to analyze their impact on the biomass gasification process. In general, the authors would like to highlight that thermochemical methods offer many advantages, such as high energy efficiency, significantly shorter reaction times, higher conversion efficiency, efficient nutrient recovery, and greater versatility toward feedstocks.

5.2. Biochemical Conversion Processes

Energy enhancement of organic substrates by biological processes is currently a very common practice. Biochemical methods include biorefinery integration, decomposition by microorganisms, consolidated fermentation, hydrolysis, and advanced combined pretreatment methods, such as ionic and deep eutectic solvents, to produce biogas, alcohols, organic acids, and gases [185]. In fact, biological technologies involve microorganisms

and their enzymes to break down cellulosic materials to produce alcohol-based biofuels (ethanol and butanol) and gaseous biofuels (biohydrogen and biomethane) [186]. Biochemical conversion pathways such as anaerobic digestion and fermentation are the two main mechanisms that are employed, starting from biomass, and will be discussed as follows.

5.2.1. Fermentation

The fermentation process is key to achieving the production of biofuels widely used as substitutes for traditional fossil fuels [187]. The microorganisms responsible for fermentation are typically bacteria or yeasts, whose goal is the conversion of sugars from organic materials, such as hexoses and pentoses, into ethanol and CO₂ under anaerobic conditions. The fermentation pathway for lignocellulosic biomass conversion is complicated and involves fractionation of the biomass by an efficient pretreatment process, followed by enzymatic hydrolysis and microbial fermentation to convert the sugars into biofuels and biochemicals. Lignocellulosic biomass consists of three main elements: cellulose (35–60%), hemicellulose (25–41%), and a polyaromatic compound, lignin (15–20%), as well as acetyl and phenolic groups, minerals, and small amounts of other compounds [188]. For effective fermentation of lignocellulosic biomass, its structure must be broken down so that polysaccharides can be converted to mono- and disaccharides through enzymatic hydrolysis. The biological function of lignin is to protect the cell wall, so it provides structural strength, impermeability, and defense against microbial action and is therefore the main obstacle in the decomposition of lignocellulosic biomass [189]. Lignin cannot be hydrolyzed or fermented, so there is a need to pretreat the LCB using different strategies. In general, as shown in Figure 6, the main pretreatment approaches include physical, chemical, physicochemical, and biological methods [190,191].

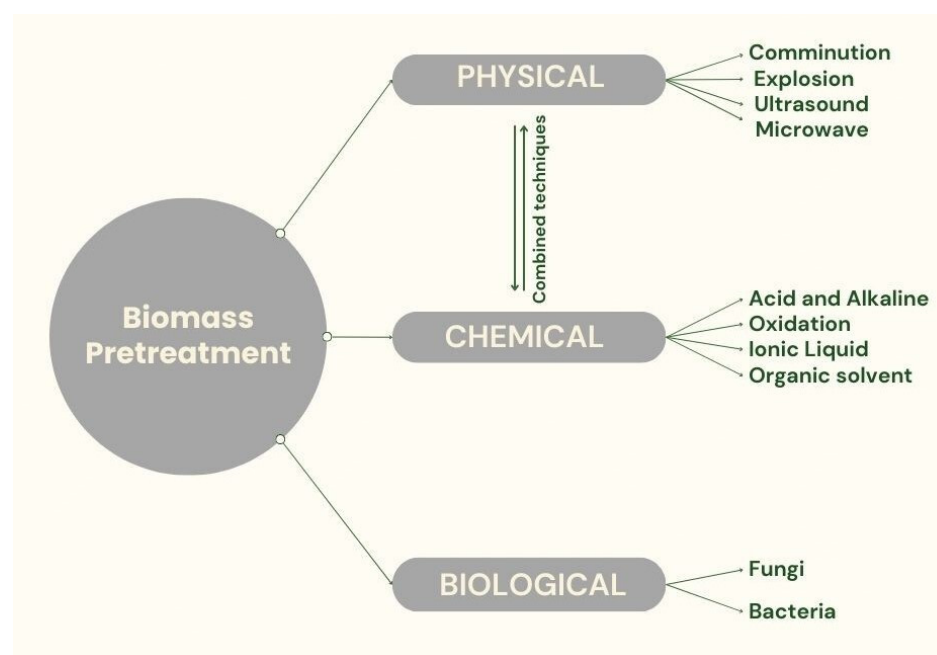


Figure 6. Outline of the different types of biomass pretreatment.

Pretreatment objectives include decreasing the crystallinity of cellulose and particle size of lignocellulosic materials, increasing the surface area of biomass, recovering hemicellulose, and modifying the recalcitrant structure of biomass (resistance to enzyme access to cellulosic materials) [191]. It must also be considered that, if not carefully monitored, pretreatment can generate undesirable by-products and microbial inhibitory components that interfere with subsequent conversion processes [192]. In the practice of procedures, strategies involving combined pretreatment processes, i.e., involving the integration of two or more pretreatment technologies, are also adopted. They have proven to be more effective

and advanced than single treatments because they promote greater accessibility of enzymes to cellulosic fibers [193]. In addition, the use of genetically engineered biomass pretreatment strategies also produced the same effectiveness, i.e., reducing LCB recalcitrance and increasing saccharification production [194]. In general, the pretreatment process should be cheap, easy to perform, and environmentally friendly, producing minimal amounts of inhibitory compounds and allowing full utilization of LCB, which results in high product efficiency and proper management of waste lignin [195]. Subsequent decomposition of the pretreated lignocellulosic components occurs by enzymatic hydrolysis (saccharification), and simpler molecules (fermentable sugars, pentoses, and hexoses) are obtained. Primarily enzymes are used to catalyze the hydrolysis of cellulose and hemicellulose, but acids and alkalis can also be used for this purpose [196]. Cellulose hydrolysis is a crucial point since cellulose microfibrils are stabilized by internal and external hydrogen bonds and surrounded by hemicellulosic polysaccharides (mannans and xylans) joined by covalent and hydrogen bonds; thus, the crucial role of the pretreatment step emerges. Enzymatic hydrolysis together with dilute acid is preferred for large sugar yields [197]. Enzymatic hydrolysis requires controlled temperature and pressure to allow enzymes to operate efficiently. Sugar-rich lignocellulosic hydrolysates can be fermented to yield as a result ethanol (0.71–0.79 L kg⁻¹ sugar), methanol (0.7 mL g⁻¹), butanol (0.4 g g⁻¹), and biochemicals [79]. Commonly used commercial microorganisms that are considered safe, resistant, and highly ethanol tolerant are *Saccharomyces cerevisiae* and *Zymomonas mobilis*. To metabolize sugars with five carbon atoms (such as xylose, mannose, galactose, and arabinose), the use of engineered microorganisms or a co-culture of two yeast strains can be employed [54]. Modifying the genetic makeup of microorganisms in order to introduce or enhance the metabolic pathways necessary for the complete fermentation of all sugars in the biomass, showing high resistance to inhibitors and tolerance to stress conditions, is the main goal of genetic modification. The fermentation process can be accomplished by batch, fed-batch, and continuous feeding. Saccharification and fermentation can be carried out separately (separate hydrolysis and fermentation—SHF) or simultaneously (simultaneous saccharification and fermentation—SSF), i.e., hydrolysis and fermentation can take place in separate reactors or in a single reactor. The potentials and drawbacks of the two fermentations are summarized in Table 4.

Table 4. Advantages and disadvantages of SHF and SSF modes of operation [198,199].

Process	Advantages	Disadvantages
Separate hydrolysis and fermentation (SHF)	Easy monitoring of pH, temperature, enzyme concentration, sugar accumulation, and inhibitor concentration	Long working times, increased inhibitory effects and use of additional equipment and processing steps
Simultaneous saccharification and fermentation (SSF)	Low risk of contamination and reduction in inhibitory effects, reduced times	Incompatibility of optimal temperature (50–55 °C) and pH (4.5–5.5)

Currently, SSF is the most popular technique on both laboratory and industrial scales in which both hydrolysis and cellulose-hemicellulose fermentation have been performed in a single reactor [200]. Once fermentation is complete, bioethanol in correspondingly high concentrations can be distilled and dehydrated (removal of water or other impurities) to obtain high-quality anhydrous ethanol, which is suitable for blending with gasoline and can be used as a transportation fuel [201].

5.2.2. Anaerobic Digestion

Anaerobic digestion, just cited above, is a bioenergy technology that can play a key role in achieving net zero emissions by converting organic matter into biogas, biomethane, and carbon dioxide [202]. The AD process consists of a series of biochemical reactions in

which bacteria break down organic matter from substrates into a gaseous mixture (CH₄, CO₂, H₂, H₂S) in the absence of oxygen. Through a community of anaerobic microorganisms, the technology transforms biodegradable biomass components into energy-rich biogas and digestate residues. Typically, the biogas produced comprises 50–75% CH₄, 30–50% CO₂, 0–3% N₂, ~6% H₂O, and 0–1% O₂, and minor impurities such as N₂, O₂, H₂, and H₂S [125]. The mechanism of AD consists of four biochemical steps, carried out by syntrophic associations of bacterial consortia [203]. Table 5 summarizes the enzymes and microorganisms involved in the various steps of the AD process.

Table 5. Microorganisms and enzymes in the process of anaerobic digestion [204,205].

AD Steps	Microbial Community	Enzymes
Hydrolysis	<i>Bacteroides, Actinobacteria, Firmicutes, Spirochetes, Proteobacteria, Eubacterium, Chloroflexi</i>	Cellulase, amylase, protease, lipase, and xylanase
Acidogenesis	<i>Enterobacter, Bacteroidetes, Firmicutes, Clostridium</i>	Acetate kinase, C-acetyl transferase, acetaldehyde dehydrogenase, and hydrogen lyase
Acetogenesis	<i>Acetobacterium, Holophaga Clostridium, Ruminococcus Sporomusa, Desulfotignum, Eubacterium, Moorella</i>	Hydrogenase
Methanogenesis	<i>Methanobacterium, Methanobrevibacter, Methanococcus Methanosarcina, Methanospirillum, Methanothermobacter, Methanosaeta</i>	Methyl-coenzyme, methyltransferase, formylmethanofuran dehydrogenase, methyltransferase, and methyl-coenzyme reductase

The AD process provides a perfectly balanced ecological environment in which organic macromolecules are degraded into soluble organic substances, with subsequent production of biogas. Figure 7 describes the steps of the AD process, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Due to the complexity of the microbial community involved, heterogeneous biomass sources can be successfully transformed into biogas during AD.

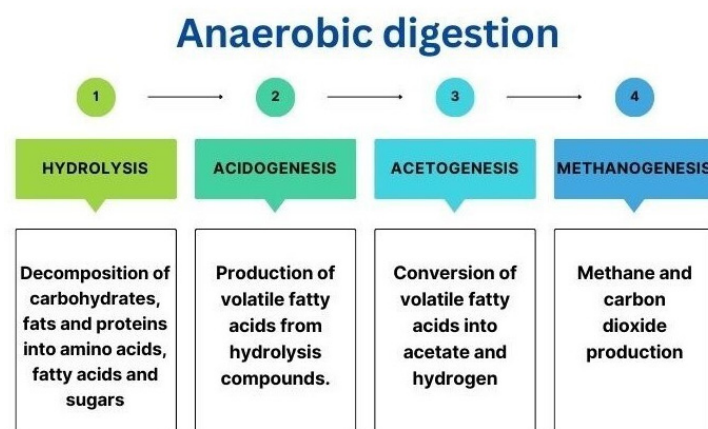


Figure 7. Stages of the AD process of biogas production.

During the hydrolysis step, insoluble organic matter is broken down into simple monomers by hydrolytic microorganisms. Proteins are converted to amino acids, lipids to fatty acids, starch to glucose, and carbohydrates to monomeric sugars [206]. In the acidogenesis step, simple and acidic sugars are converted to volatile fatty acids (VFAs) and alcohols and consequently converted to acetate, CO₂, and H₂ in acetogenesis. In the

last stage, acetate and H_2 are converted to CH_4 and CO_2 by methanogenic bacteria. The methanogenesis step needs attention because it is a critical step in the anaerobic digestion process [207]. This is the slowest reaction in the process and is strongly influenced by operating conditions. It is important to monitor parameters such as pH, temperature, substrate characteristics, carbon-to-nitrogen (C/N) ratio, organic loading rate (OLR), hydraulic retention time, solids retention time (SRT), and volatile fatty acids to optimize the performance of biogas plants and maximize production. Proper temperature, pH, a strong inoculum/substrate ratio, good mixing, and small particle size are important factors to achieve an effective and efficient AD process [206]. A wide range of biodegradable substrates as feedstock, including organic, food and animal wastes, wastewater, and crop residues, can be used to produce biogas [208]. Substrates rich in lipids and proteins have a higher potential for methane yield [209]. Again, the use of lignocellulosic biomass as a substrate has gained much attention due to its wide availability and ability not to compete directly with food or feed production. Despite this, the hydrolysis step in LCB turns out to be the limiting factor for this substrate and the process itself, as it slows down its speed. In this regard, advances are being made in optimizing hydrolysis through the use of physical, thermochemical, and biological pretreatments [210]. During biogas production, certain additives (nanoparticles, activated carbon, trace metals, chloride, and catalysts) can be added to the digester to improve biogas production [211]. In biogas production, the ratio of energy input to energy output can be as high as 28.8, indicating higher efficiency of this technology compared with other biological and thermochemical technologies for energy production [212]. The anaerobic digestion process can be conducted at a very narrow pH range (usually between 6.8 and 7.2) and under different thermal regimes, i.e., under psychrophilic ($<20\text{ }^\circ\text{C}$), mesophilic ($20\text{--}45\text{ }^\circ\text{C}$), or thermophilic ($45\text{--}65\text{ }^\circ\text{C}$) conditions [107]. The C/N ratio of raw materials reflects nutrient levels and is therefore critical for the growth of microorganisms and the effectiveness of the process [213]. In order to meet the different nutritional needs of anaerobic microorganisms and promote biogas production, it is necessary to combine a variety of organic substrates. In this regard, anaerobic co-digestion (AcoD) is an excellent method for the simultaneous management of two or more organic materials, including solids and liquids. Co-digestion compared to mono-digestion offers greater system stability and higher methane yield through the synergistic effects of a more diverse microbial community, greater nutrient balance (particularly C/N ratio), and trace element supplementation [214]. Co-digestion of animal manure with various different biomasses has been shown to lead to optimization of biogas production and stabilization of the AD process [209]. This combination improves the conversion of other biomasses and waste feedstocks into biogas and increases their production levels through a balanced supply of micronutrients. Biogas produced through the AD process can be used for a variety of purposes, such as heat production by direct combustion, power generation, or as an alternative to fossil fuels in the transportation sector [215]. To convert biogas into electricity, electricity and heat units can be used simultaneously, or a combined heat and power (CHP) unit can be used [216]. In addition, biogas can be converted into biomethane, which has a chemical composition similar to that of natural gas [217]. In fact, its use as a substitute for natural gas has received considerable interest. The conversion of waste biomass can generate up to 10,700 TWh of bioenergy per year, accounting for 10% of global final energy consumption and 27% of global natural gas supply [202]. Before biogas can be used as a substitute for natural gas, the impurities present (carbon dioxide, hydrogen sulfide, and water vapor) must be removed. Separation of these components is necessary to avoid problems from an operational point of view, as they could cause corrosion of contact materials or damage process equipment and materials of construction. After separation, the final product, called biomethane, consists of CH_4 (95–99%) and CO_2 (1–5%) and no trace of H_2S [218]. Biogas upgrading technologies include variable pressure adsorption, chemical purification, washing with water, amines or organic solvents, membrane separation, and cryogenic separation [219]. The appropriate technology option for biogas upgrading depends on the end use, economic aspects, and the efficiency of the process itself. In addition

to its role in reducing pollution and generating biogas, AD produces useful fertilizers as an integral part of the resource recycling process. In fact, digestate is the co-product of the AD process and can be applied in agriculture as a fertilizer to supplement nitrogen, phosphorus, and potassium in soils. The composition of digestate depends mainly on the quality of the raw material and the various processing steps. The multiple benefits of using digestate are gaining more and more recognition and are related to the promotion of sustainable development and circular economy, also finding applications in animal husbandry, aquaculture, and algae production [220]. However, improper management of digestate creates a serious environmental problem and legal issues if it is disposed of without proper treatment [221]. Biogas production through the process of anaerobic digestion is a central element of sustainability, as it offers versatile solutions for converting a large number of waste materials into a valuable energy resource [222]. This not only makes it possible to enhance organic wastes and refuse to maximize biomass utilization and facilitate resource recycling and nutrient recovery, but also facilitates the transition to a more sustainable, low-carbon economy.

5.2.3. Economic and Sustainability Future Perspectives

The economic feasibility of biofuels requires several considerations, such as costs of production (i.e., direct and indirect), technological advancements, government policies, market dynamics, and environmental impacts.

Feedstock, its supply, utilities, and labor are the greatest direct costs for the first generation of biofuels. Indirect costs include environmental impacts and the following consequences on human health. Moreover, the energy return on investment (EROI) and resource use efficiency are decisive for long-term sustainability.

The fulfillment of both economic feasibility and long-term sustainability is limited by several factors. For example, inefficient biomass production can contrast with biofuel production, an unsatisfactory value of photon-to-biomass conversion efficiency (PBCE) can limit productivity and, thus, the maximum achievable yield. In addition, environmental challenges in biofuel production (i.e., greenhouse gas emissions, air pollution, soil and water resources, biodiversity) should be considered. For this reason, the life cycle assessment (LCA) approach is used to assess environmental impacts and adapt the process of emission reduction during biofuel production [72]. At present, many companies involved in biofuel production take life cycle analysis (LCA) to assess environmental impact very seriously in order to make decisions aimed at optimizing the process, paying particular attention to decreasing emissions during biofuel production [223].

However, there are a limited number of studies that assess the long-term economic viability of biofuels. For example, a long-term levelized cost of energy (LCOE) estimation was carried out for biofuels in China. The use of a probabilistic model to calculate the LCOE suggested that biofuel technologies will gain economic feasibility and competitiveness in the energy market around 2025–2030 [223]. In fact, an increase in the total biofuel demand from 23% to 200 billion liters by 2028 is expected, with renewable diesel and ethanol accounting for two thirds of this growth, whereas biodiesel and biofuel represent the remaining part (IEA report). Most of the new biofuel demand comes from Brazil, Indonesia, and India compared to the European Union, the United States, Canada, and Japan where volume growth is limited by the tendency to adopt electric vehicles, high biofuel costs, and technical limitations (Lea report). Furthermore, an estimation of transport sector oil demand reduction by near 4 mboe/day by 2028 is predicted.

The socio-economic factors of biofuels are related to fuel demand, aimed at promoting social and economic gains and benefits, as well as providing environmental benefits if managed appropriately. In fact, biofuels present multiple employment opportunities, including biomass cultivation and harvesting, transportation and handling, plant management, equipment manufacturing, and maintenance. In addition, biofuels research and development can lead to innovations that improve the production efficiency and sustainability of technologies, reducing environmental impacts. In this way, biofuels diversify

energy sources and contribute to greater energy security, thereby reducing dependence on fossil fuels. Balancing economic, social, and environmental aspects is crucial to ensuring a sustainable energy future. It is critical to take advantage of available opportunities and find sustainable solutions to environmental challenges to promote socio-economic progress.

6. Conclusions

Environmental problems caused by population growth, industrialization, and over-exploitation of resources and fossil fuels are now of global concern. This has led, over the years, to the continuous search for alternative energy sources. In the current scenario, biomass is considered the main emerging alternative to fossil fuels and is capable of producing solid, liquid, and gaseous biofuels, mainly through thermochemical and biochemical technologies. This article examined the potential of biomass and biofuels as a sustainable alternative to achieve zero carbon emissions, including developments in terms of progress and sustainability. Currently, interest in biofuels is steadily growing among the scientific community. This phenomenon is mainly due to the current environment of rising oil prices and concerns about greenhouse gas emissions and global energy security. The most common biofuels are bioethanol and biodiesel, but biogas, biomethane, and bio-oil also represent valid and reliable alternative energies. Biodiesel and bioethanol have long been considered the fuels of the future, as they are considered suitable candidates to replace gasoline. The United States and Brazil have played a significant role in the development of the transportation sector, mainly as an alternative to fossil fuels, and have also contributed to significant milestones in reducing carbon emissions. The United States has allocated a significant portion of agricultural land to crops for biodiesel production, while Brazil has used sugarcane as a feedstock to produce ethanol. Biofuels have proven to be one of the most effective ways to decarbonize the transportation sector, with global production and consumption continuing to grow. Indonesia, China, Germany, and India are also investing in biofuel production and use to address environmental and energy security issues, but strategies and levels of adoption vary. Similarly, biogas and biomethane are also considered the centerpiece of the circular economy, not least because of the important advantage of being able to be stored and used on demand. Comparisons of different types of biofuels (first, second, third, and fourth generation) have shown their importance in achieving sustainable development goals. However, they present challenges and critical issues, such as competition to food crops, consumption of agricultural land, and energy use in the production process. To be a viable alternative to fossil fuels, advanced biofuels must offer environmental benefits, positive net energy gains, and be produced without compromising the food supply. It is critical to strike a balance between biofuel production and food production to ensure global food security. Technological advances and innovation in biofuels are making production processes increasingly efficient and cost-effective. New cultivation techniques, along with more efficient conversion processes, are helping to reduce production costs and improve the competitiveness of biofuels relative to fossil fuels. Assessing the costs associated with transportation and storage is also crucial to the competitiveness of various energy carriers. Careful planning can ensure maximum energy efficiency and environmental sustainability. Future scientific research efforts need to continue to optimize biofuel production, incorporating circular economy principles to ensure sustainability and their use, and assessing environmental impacts so that sustainability goals can be met. As technology advances and production costs decrease, biofuels will have a greater chance of large-scale deployment.

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