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Review

Comparative Review on the Production and Purification of Bioethanol from Biomass: A Focus on Corn

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Abstract: In the contemporary era, conventional energy sources like oil, coal, and natural gas overwhelmingly contribute 89.6% to global CO_2 emissions, intensifying environmental challenges. Recognizing the urgency of addressing climate concerns, a pivotal shift towards renewable energy, encompassing solar, wind, and biofuels, is crucial for bolstering environmental sustainability. Bioethanol, a globally predominant biofuel, offers a versatile solution, replacing gasoline or integrating into gasoline–ethanol blends while serving as a fundamental building block for various valuable compounds. This review investigates the dynamic landscape of biomass generations, drawing insightful comparisons between the first, second, third, and fourth generations. Amid the drive for sustainability, the deliberate focus on the initial generation of biomass, particularly corn, in bioethanol production is grounded in the current dependence on edible crops. The established utilization of first-generation biomass, exemplified by corn, underscores the necessity for a comprehensive examination of its advantages and challenges, allowing for a nuanced exploration of existing infrastructure and practices. To produce bioethanol from corn feedstock, various milling methods can be employed. Thus, this paper delves into a comparative assessment of dry-milling and wet-milling processes scrutinizing their efficiency, environmental impact, and economic feasibility.

Keywords: corn; bioethanol production; clean energy; energy efficiency; sustainability

Citation: Assaf, J.C.; Mortada, Z.; Rezzoug, S.-A.; Maache-Rezzoug, Z.; Debs, E.; Louka, N. Comparative Review on the Production and Purification of Bioethanol from Biomass: A Focus on Corn. *Processes* **2024**, *12*, 1001. https://doi.org/10.3390/pr12051001

Academic Editor: Cunshan Zhou

Received: 10 April 2024
Revised: 3 May 2024
Accepted: 12 May 2024
Published: 15 May 2024

1. Introduction

Ethanol (C_2H_5OH), commonly referred to as ethyl alcohol, is a colorless, volatile liquid with flammable properties when found at standard room temperature [1]. Aside from its role as a potential fuel source, ethanol serves diverse purposes, including acting as an antiseptic, a solvent, a psychoactive substance, and a building block for various organic compounds like ethylene and acetaldehyde [2,3].

There are numerous factors supporting ethanol's application as an alternative fuel, including (a) its origin from renewable agricultural resources like corn, sugar, and molasses, as opposed to finite petroleum derivatives; (b) its lower toxicity compared to alternative alcohol-based fuels; and (c) the by-products resulting from incomplete ethanol oxidation (such as acetic acid and acetaldehyde) being less hazardous than those formed by other fuel alcohols [4,5].

The term “biofuel” comprises liquid or gaseous fuels such as bioethanol, biogas, and biodiesel, derived from biomass materials. These fuels are primarily used in the transportation sector but are also commonly employed for heat production, as demonstrated in Table 1 [6]. Biofuels offer a range of notable benefits. Firstly, they are readily accessible from widely available biomass sources [6]. Secondly, they establish a balanced CO_2 cycle during combustion [6]. Thirdly, they hold substantial potential for environmentally friendly applications [7–10]. Fourthly, their utilization brings about a multitude of advantages for the environment, economy, and consumers [7–10]. Lastly, biofuels exhibit biodegradability, which contributes to sustainability in several ways, including reduced environmental impact, improved air quality, mitigation of climate change, and promotion of a circular economy [7–10].

Bioethanol, a liquid biofuel, can be manufactured using various biomass sources and conversion methods. The primary biomass feedstock for producing fuel ethanol is sugarcane, predominantly in tropical regions like India, Brazil, and Colombia [11]. Conversely, in regions such as the United States, European Union, and China, corn serves as the dominant feedstock for ethanol production [11]. The production of ethanol derived from sugar crops like sugarcane and sugar beet constitutes approximately 40% of the total bioethanol output, while starch crops contribute to nearly 60% of the corresponding production [12].

Table 1. Types of biofuels.

Types of Biofuel	Method of Production	Effect of Biofuel on the Environment	Biofuel Blends	References
Biodiesel	Transesterification	- Decreases greenhouse gas emissions up to 86% - Non-toxic - Biodegradable	Blended with petroleum-based diesel with different percentages: - B5 (up to 5% biodiesel) - B20 (6% to 20% biodiesel)	[13,14]
Biobutanol	Fermentation of sugars	Sharply decreases the PM emissions	Exists in several percentages of biobutanol blends with gasoline: 12.5% or 16%	[15,16]
Biogas	Anaerobic	Reduces global CO_2 emissions by 18–20%	Biogas blending offers an option to decarbonize the gas network	[17,18]
Bioethanol	Fermentation	Produces fewer emissions of particulates, sulfur dioxide, and air toxics than fossil fuel when burned	Bioethanol-petroleum blends also generally result in lower emissions relative to fuels that do not contain bioethanol	[19]

2. Bioethanol Sources

2.1. First Generation

Biofuels of the first generation are produced using two categories of consumable raw materials, namely feedstocks derived from starch and sugar [20]. The process that allows the ethanol production from sugarcane is relatively simple; the sugarcane is crushed in water to remove sucrose, which is then purified to produce ethanol [21]. On the other hand, corn requires starch hydrolysis before the sugars can be fermented into ethanol. The co-product of this fermentation process, known as distiller dried grains with soluble (DDGS), can be used as animal feed due to its high nutritional value, making it a valuable commodity in the market [22,23]. However, the first-generation biofuels, such as those derived from corn, sugarcane, or wheat, often compete with food production [24,25]. This competition arises because these crops are used both for fuel and food, leading to concerns about resource allocation and potential impacts on food security [26]. Thus, it remains imperative to conduct a thorough study to determine the optimal feedstock from first generation of biomass (corn, wheat, sugarcane, cassava, and sweet sorghum) for bioethanol production [25,27].

The conversion rates are as follows: corn to starch at 69%, wheat to starch at 66%, and cassava to starch at 25% [28]. Furthermore, the conversion rate of corn to bioethanol is notably superior, at 410 L/ton, surpassing both wheat (390 L/ton) and cassava (150 L/ton) conversions [28]. In terms of bioethanol yield, cassava demonstrates the highest potential, yielding 6000 kg/ha/year, followed by corn with a yield of 2050 kg/ha/year, while wheat lags behind with a yield of 1560 kg/ha/year [28]. Considering production costs, corn offers a cost range of 250–240 USD/m^3, wheat falls within the range of 380–480 USD/m^3, and cassava emerges as the most expensive option at 700 USD/m^3 [28].

Table 2 provides valuable insights into the distribution of first-generation biofuel plants, their capacity utilization, and the feedstocks used in different countries, specifically the USA, Brazil, the EU, China, and India [29].

Table 2. Bioethanol production from first-generation feedstock in different countries.

Country	Number of 1st-Generation Plants	Capacity Used (%)	Feedstocks (×1000 Mt)	References
USA	208	80	Corn: 123465	[30]
Brazil	360	67	Corn: 5995 Sugarcane: 326630	[31]
EU	57	58	Corn: 6350 Sugar: 7450	[31,32]
China	18	49	Corn: 7100 Cassava: 1000	[31]
India	220	85	Molasses: 6407	[31]

In light of these comprehensive considerations, it is unmistakably clear that corn emerges as the most economically sound and high-yield option for raw material in the context of bioethanol production [28].

2.2. Second Generation

Lignocellulosic biomass is primarily categorized into three groups: homogeneous materials, like white wood chips, which have minimal bark impurities and a high cellulose content, typically valued in the range 100–120 USD/ton; quasi-homogeneous such as agricultural and forest residues priced at 60–80 USD/ton; and non-homogeneous, including municipal solid wastes, with a price between 0 and 60 USD/ton [22]. In addition, the lignocellulosic biomasses are hemp, rice straw, corn stalks, sugarcane bagasse, and wheat straw [33]. Therefore, lignocellulosic biomass is inexpensive and widely available [22]. Indeed, the great advantage of second-generation bioethanol is that, in case the process was implemented on large scale, it would virtually solve the issue of competition between human food and energy production while also being highly sustainable when the energy is produced from waste materials [34]. Lignocellulosic biomass sources are very resistant to chemical and biological breakdown due to their strong covalent bonds, van der Waal bonds, and hydrogen bonds [35].

2.3. Third Generation

Microalgae (phytoplankton) float on the water's surface due to their high lipid content. Their carbohydrate content can reach 70% under specific conditions [36,37]. As for macroalgae, known also as seaweed, they are found adhering to rocks or other structures, and their carbohydrate content is found at 25–50% in green algae, 30–60% in red algae, and 30–50% in brown algae [37]. Microalgae, being able to thrive in unfertile lands and utilizing brackish, waste, or marine water, present a cultivation method that avoids competition with resources for traditional food production, offering a more environmentally sustainable alternative to extensive crop cultivation [38,39]. Consequently, microalgae cultivation provides an opportunity to redirect portion of unsustainable farming and fishing practices toward unproductive regions [38,39].

2.4. Fourth Generation

"Algae-to-biofuels" technology is used in the third and fourth generations of biofuel production. The former involves processing algal biomass for biofuel production, while the latter involves metabolic engineering of algae to produce biofuels from oxygenic photosynthetic microorganisms [40]. These microorganisms undergo genetic modification to enhance CO_2 absorption for photosynthesis, establishing an artificial carbon sink and boosting biofuel production [41]. Numerous algae strains, including *Chlamydomonas reinhardtii* sp., *Phaeodactylum tricornutum* sp., and *Thalassiosira pseudonana* sp., have been genetically altered to increase growth rates and adaptability in nutrient-poor environments [41]. This modification offers environmental benefits such as CO_2 sequestration, acting as a medium for wastewater treatment and reducing greenhouse gas emissions [42–44]. The fourth generation aims for minimal environmental impact compared to previous generations, although ongoing research is in its early stages [45]. Consequently, much of the existing literature focuses on studying the environmental effects of the gene modification process [42,44].

2.5. Comparison between Different Generations of Biomass

The comparison between different generations of biomass in Table 3 reveals significant differences in their respective methodologies, each presenting distinct advantages and limitations. The first generation heavily relies on food crops for biofuel production, which raises concerns about sustainability and food security [41,46,47]. In contrast, the second and third generations offer higher sustainability levels by utilizing non-edible crops and algal biomass, respectively. Thus, these generations reduce the dependence on food crops and demonstrate higher CO_2-capture abilities [37,48]. However, they require more advanced technologies and face challenges such as recalcitrant structures of feedstock or limited investments [48]. Moving forward to the fourth generation, it represents an innovative approach utilizing engineered biomass but is still in its early developmental stages [26]. It boasts high biomass and production yield, along with the capability to eliminate CO_2, yet its implementation requires advanced methods and incurs high bio-reactor costs [26]. Moreover, it necessitates significant investment at the early stages of development [48]. Despite these challenges, the first generation enjoys a widespread adoption due to its simpler conversion process [48]. The comparative analysis of bioethanol production costs reveals a clear advantage for first-generation bioethanol, with the lowest cost ranging from USD 0.4 to USD 0.5 per liter. This underscores the economic efficiency of utilizing readily available edible crops. Second-generation bioethanol, produced from non-edible crops, incurs a moderate increase in costs, ranging from USD 0.7 to USD 2 per liter. However, the transition to third-generation bioethanol, utilizing algal biomass, introduces a substantial leap in production costs, ranging from USD 10 to USD 20 per liter. Notably, fourth-generation bioethanol, utilizing engineered biomass, is still in the developmental phase, and its production costs remain undetermined. These findings collectively underscore the importance of first-generation bioethanol as a cost-effective pathway for sustainable biofuel production.

Table 3. Comparison between the four generations of biomass.

Comparative Elements	First Generation	Second Generation	Third Generation	Fourth Generation	References
Feedstock sources	Edible crops (sugar beet, sugar can, wheat, corn)	Non-edible crops (wood, grasses, organic waste, agricultural and forestry residues)	Algal biomass (macroalgae, microalgae)	Engineered biomass (engineered crops)	[41,46,47]
Land usage for cultivation	Arable land	Arable and marginal lands	- Seawater - Fresh water - Wastewater	Non-arable land	[49,50]
Conversion technologies	- Sugar extraction - Fermentation - Distillation	- Pretreatment - Hydrolysis - Fermentation - Distillation	- Hydrolysis - Fermentation - Distillation	Algal metabolic engineering for enhanced carbon capture, cultivation, harvesting, and conversion processes	[51–53]
Conversion process	Easily converted to ethanol	Requires more advanced technology	Limited investments and difficulties in process design	Requires an advanced method	[48]
Environmental impact	High contribution to the mitigation of CO_2	- GHG savings - Utilizes food wastes as feedstock	Enhanced CO_2-capture ability	High CO_2-capture ability	[37,48]
Main advantage	Relatively simple conversion process	- Reduces the amount of waste - No competition with food resources	Increased efficiency and sustainability	- High biomass and production yield - Capability to eliminate CO_2	[48–50]
Main disadvantage	Competition with food supply	Recalcitrant structures of the feedstock	- Limited investments - Difficulties in process design	- High bio-reactor cost - Requires high investment at early stage	[26]
Production cost	~0.4–0.5 USD/L	~0.7–2 USD/L	~10–20 USD/L	_	[54]

3. Bioethanol

3.1. Global Production

Over the past two decades, global ethanol production has witnessed a substantial increase, rising from 17,062,000 mt to 108,414,000 mt [55]. In 2015, the world produced 97,280,000 mt of bioethanol, with the United States contributing 56,278,000 mt and Brazil 26,942,000 mt [56]. Currently, the USA and Brazil accounted together for 85% of the world's bioethanol production [56]. This surge can be attributed primarily to the growing demand for environmentally friendly fuels and reduced reliance on fossil fuels [56]. Ethanol production is expected to further rise to 135,014,000 mt by 2024 [17], with projected consumption reaching approximately 140,539,532 mt by 2029 [57].

Biothanol has the potential to decrease reliance on petroleum imports, enhancing a nation's balance of payments and energy security [58]. Cost-effective bioethanol production not only meets fossil fuel demand but also mitigates price hikes, boosting feedstock demand [59].

3.2. Characteristics, Limitations, and Advantages

The data outlined in Table 4 offer a thorough comparison of the fuel properties of bioethanol and gasoline, shedding light on ethanol's higher heat of vaporization. This means that more energy is needed to evaporate the fuel, leading to a decrease in engine temperature [60]. Consequently, it has the potential to enhance knock resistance by reducing the likelihood of auto-ignition in a cooled engine. This feature leads to an increased volumetric efficiency when ethanol is blended with gasoline as opposed to using pure gasoline, resulting in a direct enhancement of power output [61–63]. Research studies have further demonstrated that a modest 5% increment in ethanol content within these blends can yield a remarkable 10% improvement in the fuels' octane rating [64].

While bioethanol offers a renewable energy alternative, its reliance on edible crops such as maize raises concerns regarding potential increases in food prices, shortages, and ethical dilemmas associated with diverting resources from the food supply chain [65]. In the future, a shift away from first-generation bioethanol production towards more sustainable alternatives may occur. Thus, many government policies, such as those outlined in the EU Renewable Energy Directive II (REDII), emphasize the promotion of advanced biofuels derived from non-food sources [66]. Consequently, while first-generation bioethanol production may persist in the near term, the long-term trend suggests a decreasing reliance on these feedstocks in favor of more sustainable alternatives [67].

Despite the negative drawback of bioethanol production competing with food, it offers numerous advantages, including combustion and engine performance [68,69]; it boasts a high octane number, which contributes to improved volumetric efficiency, and it provides an ample oxygen supply for thorough combustion [70–73]. Bioethanol also plays a role in reducing evaporative emissions, exhibits a high laminar flame propagation speed, enhances thermal efficiency and engine torque output, and enables the use of high compression ratios without engine knocking, thus resulting in cleaner emissions [74,75]. Bioethanol readily blends with gasoline and is commonly used as an oxygenated component, making it an environmentally friendly alternative [76,77]. Therefore, bioethanol is less toxic than gasoline, further enhancing its appeal as a sustainable fuel option [76,77].

Table 4. Physical and chemical properties of gasoline and bioethanol.

Fuel Properties	Gasoline	Bioethanol	References
Molecular formula	~$C_8H_{15.6}$	C_2H_6O	
Density at 15 °C (kg/m^3)	720–775	792	[78,79]
Boiling point at 1.013 bar (°C)	25–210	78.4	[79,80]
Octane number, MON/RON	85/95	89.7/108.6	[68,69]
Heat of vaporization (kJ/kg)	289	854	[60]
Energy density (MJ/kg)	45	26	[81,82]
Composition C/H/O (%mass)	87.4/12.6/0	52.18/13.04/34.7	[83,84]
Molecular weight (kg/kmol)	98	46.070	[85]

3.3. Diverse Applications

Bioethanol holds a substantial market demand of 86 million metric tons/year, primarily employed as a fuel additive [86]. Bioethanol also serves as a vital feedstock for bio-based chemicals through two distinct conversion pathways: polymerization and oxidation [86]. Polymerization leads to the production of industrial plastics such as polyethylene and polypropylene [86]. In contrast, the oxidation process results in polyethylene terephthalate and ethylene glycol derivatives [86]. The latter have various applications, including use as a coolant, solvent, and antifreeze and in the production of textile fibers [86] (Figure 1).

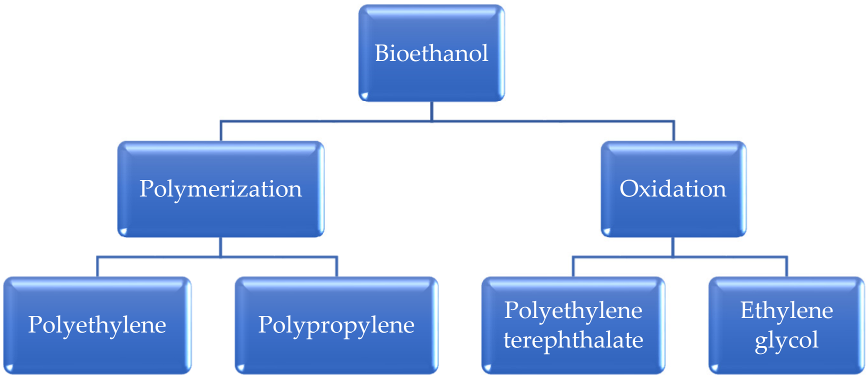

Figure 1. Chemical derivatives of bioethanol.

4. Ethanol Production from Different Feedstocks

Ethanol production encompasses diverse methods utilizing both non-renewable resources like coal and natural gas and renewable sources such as biomass. In this section, each of these methods are detailed, exploring their processes and implications.

4.1. *Production of Synthetic Ethanol from Non-Renewable Resources*

The production of synthetic ethanol from non-renewable resources such as coal and natural gas includes coal gasification and natural gas steam reforming, passing by syngas production, in addition to ethylene catalytic hydration. These methods, as depicted in Figure 2, are discussed in this section.

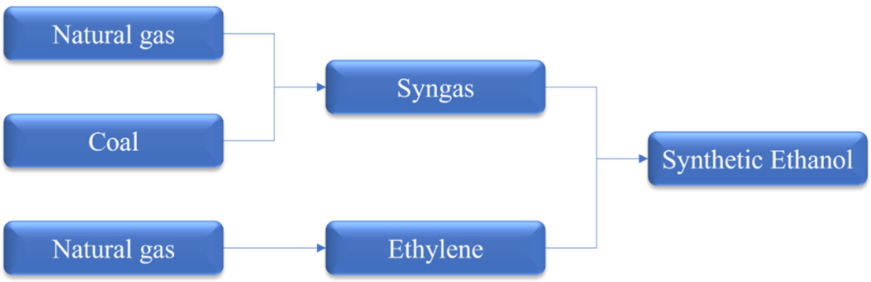

Figure 2. Production of synthetic ethanol from natural gas and coal.

4.1.1. Production of Synthetic Ethanol through Gasification Process

The gasification of coal is a crucial process that produces a synthetic gas consisting of more than 50% H_2 and CO, where CO is converted into ethanol [87]. This synthetic gas, composed of CO, CO_2, and H_2, holds significant promise, as it can serve as a valuable substrate for the biological synthesis of fuels and chemicals [88]. To transform CO into ethanol through the fermentation process, a specific type of bacteria should be used. For instance, bacteria such as *Rhodospirillum rubrum* effectively harness CO and water to generate H_2 and CO_2 [89]. Furthermore, various other microbial species, including *Peptostreptococcus productus* [90] and *Eubacterium limosum* [91], exhibit the capability to transform CO, CO_2, and H_2 into acetate. Notably, *Butyribacterium methylotrophicum* has the capacity to produce butanol from CO [92], while *Clostridium ljungdahlii* can efficiently yield ethanol from the combination of CO, CO_2, and H_2 [42], as shown in Equation (1).

$$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2 \tag{1}$$

These examples illustrate how gasification byproducts can be directly utilized by microorganisms in the biological production of valuable biofuels and chemicals, offering an environmentally friendly and sustainable avenue for resource utilization [42].

For ethanol production from coal, there are three basic steps in this procedure, as shown in Figure 3. First, the thermal gasification step, at a temperature up to 1200 °C in a low oxygen atmosphere, transforms organic materials into simple CO, CO_2, and H_2 gases [93]. Second, carbon monoxide is converted to ethanol during fermentation. Finally, ethanol is separated from hydrogen and water during purification [94].

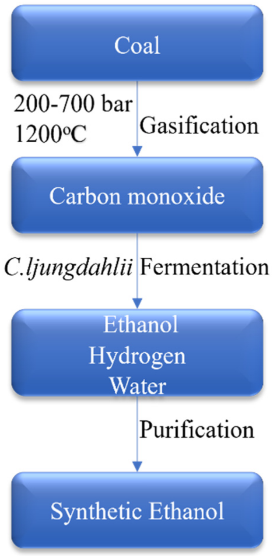

Figure 3. Production of synthetic ethanol from coal.

4.1.2. Production of Synthetic Ethanol from Natural Gas

Natural gas is subjected to steam reforming to produce syngas at temperatures of 250 °C and pressures of 20 bar [95]. Subsequently, the syngas undergoes catalytic conversion into methanol within the temperature range of 250–300 °C and a pressure range of 50–100 bar [96]. This is followed by methanol carbonylation at 600 bar and 250 °C [84]. Finally, acetic acid is hydrogenated to synthetic ethanol at pressures ranging from 140 to 300 bar and temperatures ranging from 200 to 300 °C, as Figure 4 shows [97]. It is important to note that the conversion from methanol to ethanol involves complex, expensive, and energy-consuming steps. Therefore, direct ethanol production from alternative feedstocks remains more economically favorable [84].

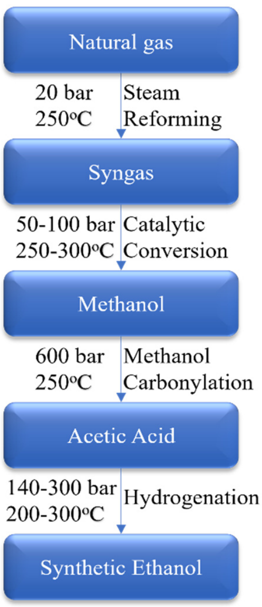

Figure 4. Production of synthetic ethanol from natural gas.

4.1.3. Production of Synthetic Ethanol from Ethylene

After sweetening, ethylene is produced through steam reforming of the natural gas at specific conditions, as shown in Figure 5 [98]. Then, the stream containing ethylene and water is heated up to 300 °C in the furnace before it enters into a packed-bed catalytic reactor at 70 bar, where synthetic ethanol is produced [99].

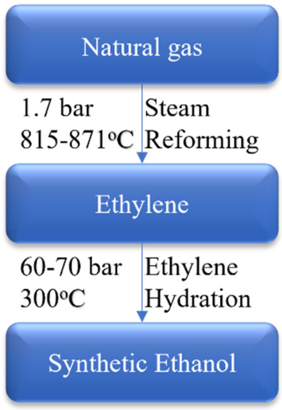

Figure 5. Production of synthetic ethanol from ethylene hydration.

The natural gas steam reforming process, yielding syngas, has a significant environmental impact, emitting about 1.93 times more CO_2 than is used as a raw material [100]. The conversion of natural gas through steam cracking to produce ethylene and ethanol introduces adverse environmental effects, including substantial greenhouse gas emissions (840 kg of CO_2 per ton of ethylene) and acidification, primarily caused by sulfur oxides (SO_x) and nitrogen oxides (NO_x) emissions, mainly from burning natural gas as an ethylene source [101]. These challenges emphasize the imperative of exploring alternative and sustainable pathways for bioethanol production to address the environmental concerns associated with the current production process.

4.2. Production of Ethanol from Biomass

Bioethanol, derived from renewable sources such as lignocellulosic biomass and waste materials, offers a locally sustainable alternative to imported fossil fuels, addressing the need for eco-friendly options amid diminishing reserves. However, it is important to acknowledge the negative effect of production through gasification processes, which involves the non-sustainability of converting half of the carbon into carbon dioxide, thus contributing to environmental concerns alongside low productivity [27,97].

Each feedstock could be produced through a specific method, as shown in Figure 6. The sugary feedstock is a class of the first generation that can be produced through fermentation after the sugar juice has been extracted [102–104]. In contrast, starchy feedstock such as corn and wheat turn into sugar through enzymatic hydrolysis even by dry milling or by wet milling. Then, the sugar undergoes the fermentation process to produce bioethanol [4,99].

Lignocellulosic materials can be challenging to break down due to their complex and rigid structure [105]. Therefore, additional steps or treatments are necessary to render them more amenable to conversion processes [105]. The first step is the pre-treatment method, which includes biological, chemical, and physiochemical treatments [105]. Then, enzymatic hydrolysis is applied before the fermentation process [33,100].

In addition, the direct conversion of lignocellulosic materials after gasification produces high amounts of methane and other hydrocarbons as by-products, which makes its commercialization challenging [106]. Algae materials also undergo hydrolysis, fermentation, purification, and recovery [107].

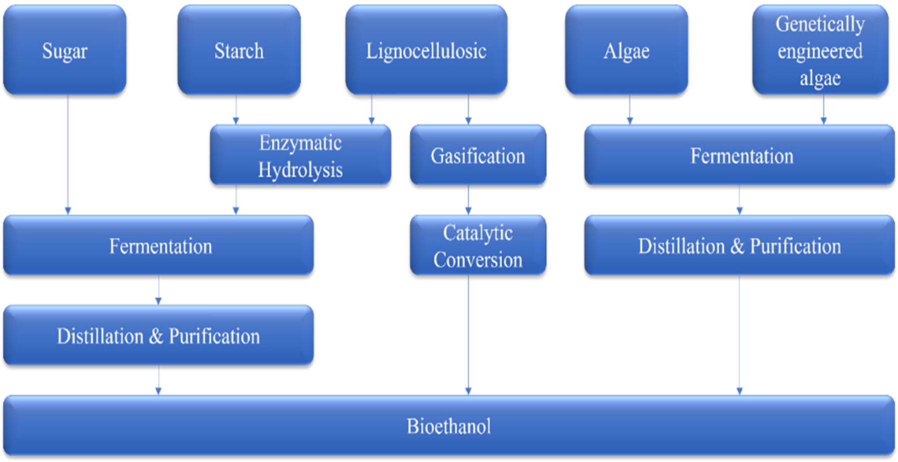

Figure 6. Bioethanol production from different generations of biomass.

5. Bioethanol Production Process

Biothanol production technologies vary significantly depending on the type of feedstock, with corn to ethanol conversion being the most mature technology. The two most common conventional methods for producing ethanol from corn are dry and wet milling [108].

5.1. Dry Milling

Corn dry-milling operations are particularly designed to manufacture fuel-grade ethanol in a "one-shot" process directly from corn kernels. The steps involved in the dry-milling process are milling, cooking and liquefaction, saccharification, fermentation, and purification [109] (Figure 7).

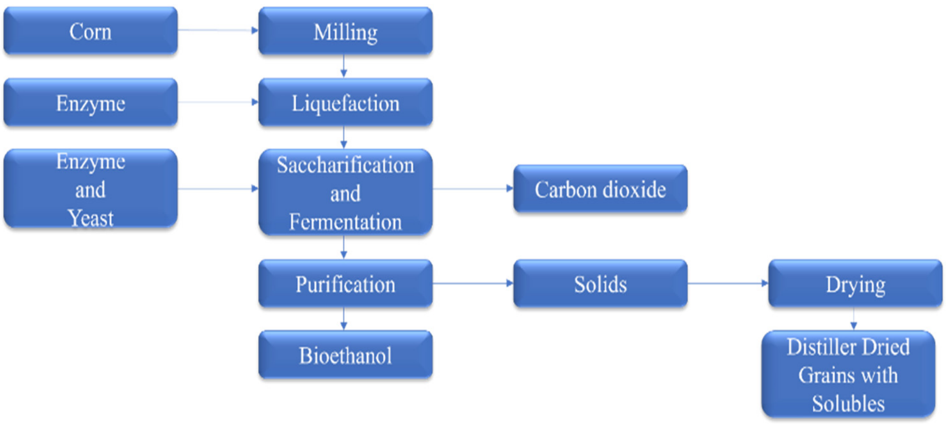

Figure 7. Dry-milling process.

5.1.1. Milling

In the dry-grind procedure, corn kernels undergo grinding within hammer mills, resulting in the formation of finely ground particles [110]. This operation serves to prepare the corn for subsequent stages by enhancing its permeability to water and enzymes [111,112].

In a hammer mill, the cereal grain is fed into a grinding chamber in which a number of hammers rotate at high speed [113]. The mill outlet contains a retention screen that holds back larger particles until they are broken down further so that there will be a known maximum particle size in the meal [114]. The screens used in the hammer mills are normally in the size range 2–4 mm [114]. When the grains are milled into powder, they are heated with water at 85 °C [4].

5.1.2. Cooking and Liquefaction

Upon acquiring corn slurry, it undergoes a cooking process facilitated by a hydro-heater [115]. This thermal treatment serves a dual purpose, elevating the temperature and concurrently reducing the bacterial content within the corn mash [115]. Subsequent to this, the cooked starch, denoted by the molecular formula ($(C_6H_{10}O_5)_n$ with $300 < n < 1000$), undergoes liquefaction at temperatures ranging between 80–120 °C and at a pH level of 6–6.5, conditions conducive to the action of α-amylase [114,116].

This choice of pH and temperature is deliberate, aligning with the gelatinization step, wherein there is a significant surge in slurry viscosity [114]. This spike is promptly mitigated as the α-amylase catalyzes the hydrolysis of starch into dextrin, as illustrated in Equation (2) [117]. The resultant dextrin exhibits a molecular formula of $(C_6H_{10}O_5)_n$, where $6 < n < 30$ [117].

$$Starch + Water \xrightarrow{\alpha-\text{amylase}} Dextrins \tag{2}$$

5.1.3. Saccharification

After cooking and liquefaction, the next step is saccharification. It is the process of dextrin hydrolysis into glucose monomers. Its optimum conditions are a temperature of 55–65 °C and a pH of 4.5 (pH of glucoamylase) [116,118]. This process involves the use of glucoamylase that cleaves both the α (1,4) and α (1,6) glycosidic bonds from dextrin ends and forms glucose [114,119–122]. The reaction involved during the saccharification is denoted as Equation (3):

$$Dextrins + Water \xrightarrow{\text{Glucoamylase}} Glucose \tag{3}$$

5.1.4. Fermentation

As the final chemical step, fermentation can be conducted by different methods, including batch, fed-batch, repeated batch, or continuous mode.

In a batch process, the substrate is introduced at the beginning without adding or removing the medium, making it a simple and flexible bioreactor system [123,124]. Although it offers benefits such as complete sterilization and easy management of feedstocks, it has drawbacks such as low productivity, high labor costs, and potential substrate inhibition [125].

Cell recycle batch fermentation (CRBF) is an effective strategy for ethanol production, reducing the time and cost of inoculum preparation [126]. Repeated-batch processes have advantages such as easy cell collection, stable operation, and long-term productivity [126]. The combination of simultaneous saccharification and fermentation (SSF) with repeated batch fermentation has been successful in some cases, but its application to lignocellulosic materials faces challenges due to the presence of residues in the fermentation medium [127–130].

Fed-batch fermentation combines features of batch and continuous modes by adding substrate without removing the medium [131]. It helps overcome substrate inhibition in batch operations and offers higher productivity, dissolved oxygen, shorter fermentation time, and lower toxicity [131]. However, its productivity is limited by feed rate and cell mass concentration [131]. Fed-batch operation has been applied successfully in non-uniform SSF systems [132].

Continuous fermentation involves constantly adding substrates, culture medium, and nutrients to a bioreactor with active microorganisms [125]. It offers higher productivity, smaller bioreactor volumes, and reduced investment and operational costs compared to batch and fed-batch systems [133]. However, there is a higher risk of contamination at high dilution rates due to incomplete substrate consumption by yeasts, thus leading to an increase in ethanol productivity and a decrease in ethanol yield per unit of substrate consumed [134].

Furthermore, Equations (4) and (5) are the main reactions involved in the fermentation process. In the initial Equation (4), glucose undergoes fermentation by yeast, yielding ethanol and carbon dioxide (1:2:2). In the subsequent Equation (5), glucose and water undergo a transformation, resulting in the production of glycerol and oxygen (1:2:2:1).

$$C_6H_{12}O_6 \xrightarrow{Yeast} 2C_2H_6O + 2CO_2 \tag{4}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2C_3H_8O_3 + O_2 \tag{5}$$

The involvement of microorganisms in sugar fermentation plays a crucial role in the production of bioethanol [135]. Certain microorganisms possess the capability to utilize glucose in anaerobic conditions, generating ethanol and carbon dioxide [136]. This characteristic has established them as potential bioagents in the history of fermentation technology [136]. The use of microorganisms, particularly yeast, in fermenting sugars is a longstanding practice in biotechnology, historically employed for the production of alcoholic beverages [137]. In contemporary times, this practice has evolved into an industrial application, specifically for the production of fuel ethanol from renewable energy sources [137].

Essential attributes of ethanologenic microorganisms designed for industrial applications encompass achieving a superior ethanol yield, surpassing 90.0% of the theoretical yield [138]. Additionally, they should demonstrate tolerance to ethanol levels exceeding 40.0 g/L, exhibit robust ethanol productivity surpassing 1.0 g/L/h, and display efficient growth in straightforward and cost-effective media [138]. Furthermore, these microorganisms are expected to thrive in undiluted fermentation broth, showcasing resistance to inhibitors while also possessing the ability to impede contaminants under diverse growth conditions, such as acidic pH or elevated temperatures [138].

Various microorganisms, including dried yeast or *Saccharomyces cerevisiae* [126,138], *S. diastaticus*, *Kluyveromyces marxianus* [139–143], *Pichia kudriavzevii* [144], *Escherichia coli* strain KO11 and *Klebsiella oxytoca* strain P2 [145,146], and *Zymomonas mobilis* [147], have been extensively examined for their potential in ethanol production from sugar juices. Among these ethanol-producing microorganisms, *Saccharomyces cerevisiae* stands out as a particularly attractive choice for fermentation [127,139]. Its appeal lies in its superior efficiency in converting sugar into alcohol, its ability to produce flocs during growth for easier settling or suspension as needed, and its high tolerance to ethanol [140]. Additionally, *S. cerevisiae* is employed in the fermentation of crop juices containing sucrose due to its capacity to hydrolyze sucrose into glucose and fructose using the invertase enzyme [127,139]. However, the optimal temperature range for *S. cerevisiae* in ethanol production is limited to 30–35 °C, prompting researchers to explore thermotolerant microorganisms [148].

Zymomonas mobilis, a Gram-negative bacterium, has been extensively researched over the past three decades for its role in fuel ethanol production from grains, raw sugar, sugarcane juice, and syrup [147]. This microorganism exhibits ethanol tolerance, higher glucose uptake, and efficient ethanol production capabilities [149,150]. It utilizes the Entner–Doudoroff pathway, employing enzymes such as pyruvate decarboxylase and alcohol dehydrogenase to convert glucose into ethanol [151]. *Z. mobilis* has a reported higher ethanol yield (97.0%) and productivity due to the production of less biomass and the maintenance of a higher rate of glucose metabolism through its ED pathway in contrast to *S. cerevisiae*, which achieves ethanol yields of only 90.0–93.0% [152]. Despite these advantages, *Z. mobilis* cannot immediately replace *S. cerevisiae* in fuel ethanol production due to its narrow substrate range [152]. Effective fermentation requires careful culture maintenance. Microorganisms commonly used in the fermentation process are heterotrophs, relying on a carbon and nitrogen source for growth and survival in the culture media [153]. Utilizing low-cost media and selecting appropriate carbon and nitrogen sources are essential for optimizing fermentation efficiency and reducing production costs. Common sources of carbon for ethanol fermentation include glucose, sucrose, maltose, and other sugars, while nitrogen sources may include peptone, yeast extract, ammonium sulfate, and other nitrogen-containing compounds. Moreover, maintaining optimal growth conditions, such as temperature and pH, further enhances microbial activity and ethanol production. Thus, without appropriate media and suitable growth conditions, obtaining a healthy inoculum for incorporating microbial cells into the fermentation broth becomes challenging [153]. The growth conditions of microorganisms vary based on their type and strain, as detailed in Table 5.

Table 5. Growth conditions of microorganisms involved in ethanol fermentation.

Name of Microorganisms	Carbon Source (g/L)	Nitrogen Source (g/L)	Growth Temperature (°C)	pH	Time (h)	References
S. cerevisiae CICC 1308	Glucose or sucrose (50)	Peptone (5)	30	5	48	[154]
S. diastaticus Y2416	Maltose (3) and glucose (20)	Yeast extract (5), peptone (5)	30	6	–	[155]
K. marxianus DMKU 3-1042	Sugar (50–80)	Ammonium sulfate (0.5)	35	4.5	72	[141]
P. kudriavzevii DMKU 3-ET15	Glucose (20)	Peptone (20)	40	6.5	48	[156]
Z. mobilis	Glucose (10) and sucrose (30)	Yeast extract (5)	30	6.5	18	[157]
Z. mobilis ATCC 10988	Glucose (20)	Ammonium sulfate (1)	30	6	24–48	[158]
E. coli KO11 and *K. oxytoca* P2	Sucrose (20)	Ammonium sulfate (2)	30	–	24	[145]

5.1.5. Purification

As known, ethanol boils at 78.4 °C, while water boils at 100 °C, but the mixture formed by their combination boils at 78.2 °C, which is lower than either of its constituents, and so, this mixture is considered as azeotropic [159–162]. The purification step in bioethanol production employs various methods like rectification, distillation, membrane separation, pervaporation, and adsorption, all of which significantly impact the final product [163,164]. Among these methods, distillation is the most commonly employed for purification, even though it consumes a substantial amount of energy [165]. Distillation works on the fundamental principle of separating mixtures based on the volatility of their components, necessitating careful monitoring of content concentration [166].

A typical distillation unit comprises several components: (1) the feed (the ethanol to be purified), (2) an energy source (typically steam), (3) overhead equipment, (4) the bottom product, and (5) a condenser [167]. However, when striving for exceptionally high-purity bioethanol while minimizing energy consumption, the system often undergoes modifications, including distillation at reduced pressures and other innovative techniques. These adjustments align with advancements in engineering technology aimed at producing premium-grade bioethanol with enhanced energy efficiency. The distillation process facilitates mass transfer between various components, functioning in a counter-current manner [168]. Given the high energy consumption associated with distillation, alternative methods for purifying ethanol from fermentation broth have emerged, including solvent extraction, membrane processes, CO_2 extraction, vapor recompression systems, and low-temperature blending with gasoline. However, these approaches are not adopted in industrial ethanol production [169].

After discussing the dry-milling steps and moving on to bioethanol purification, another conventional method, namely wet milling, is elaborated upon.

5.2. Wet Milling

The traditional wet milling of corn is a procedure designed to extract and refine starch along with various byproducts [170]. The corn wet-milling industry originated in the United States in 1844 when Thomas Kingsford, associated with William Colgate and Company in Jersey City, NJ, introduced an innovative alkali-based process for extracting starch from maize [171].

The traditional wet-milling process comprises grain handling, steeping, separation, and product recovery, as illustrated in Figure 8 [172]. First of all, shelled corn undergoes initial mechanical cleaning to eliminate unwanted materials such as cobs, sticks, husks, meal, and stones [172]. Next, the cleaned corn is introduced into “steep” tanks, where it is soaked in diluted sulfuric acid at around 52 °C for 24 to 48 h [172]. This steeping process serves to soften the kernels, break down protein-binding starch particles, and extract soluble components [172]. Then, the process involves emptying the steep tank filled with swollen maize [172]. The maize is released into a rapid water stream, called sluice water, which transports the kernels to the grinding mill or de-germinating mill [172]. To conserve water, the sluice water is collected and reused after being filtered through a screen [172]. After that, the soaked maize kernels are coarsely ground into a slurry using disk mills to separate the maize germ from the endosperm and hull [172–174]. The slurry is then passed through a two-stage hydrocyclone system to recover the maize germ, which is subsequently dried and typically sold for human consumption after purification in oil mills [172–174]. Any leftover maize germ meal is used as livestock feed [172–174]. Once the germ is separated, the remaining components of maize, including maize fiber, maize starch, and maize gluten, are processed further [172,175,176]. They are finely ground using plate or single-disk mills. Maize fiber is extracted from the fine slurry through screening and centrifugation, followed by washing and drying [172,175,176]. The maize starch and maize gluten are then separated based on their density differences using a disk-nozzle centrifuge. Further starch washing in hydrocyclones removes additional maize gluten [172,175,176]. A mill stream thickener dehydrates the maize gluten, which is further processed through a vacuum belt filter and dried using a ring dryer [172,175,176]. Finally, after starch formation, the steps followed are the same as that of dry-milling process including liquefaction, saccharification, fermentation, and purification [177].

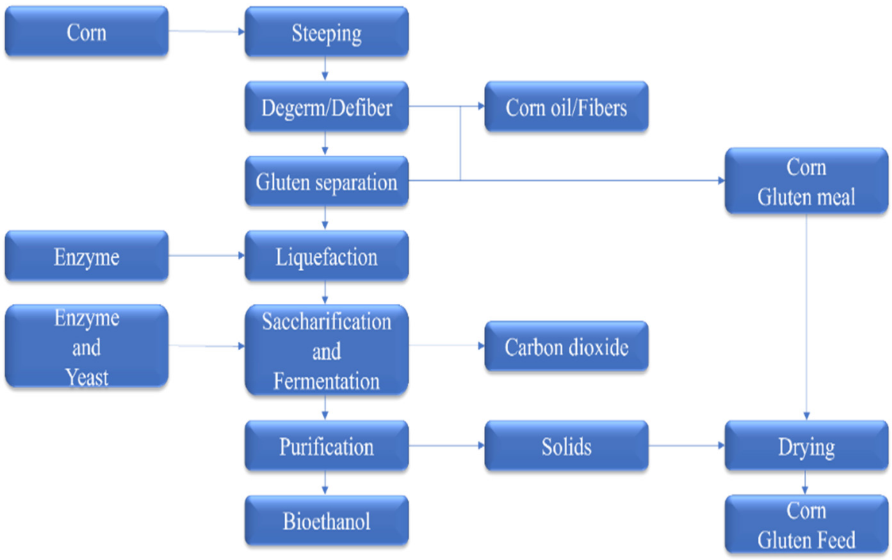

Figure 8. Wet-milling process.

5.3. Advantages and Disadvantages of Wet and Dry Milling

Wet-milling technology was pioneered approximately 150 years ago [178]. In the wet-milling process, corn kernels undergo steeping to extract their various components, resulting in a greater quantity of by-products like corn oil, corn gluten meal, and starch as shown in Table 6 [179]. The starch is subsequently subjected to enzymatic hydrolysis and fermentation to produce ethanol [4,174]. In contrast, dry milling skips the steeping phase and instead grinds the entire corn kernel before following a similar set of steps as wet milling to produce ethanol [110]. Therefore, most commercial ethanol production facilities prefer dry milling due to its lower capital costs, attributed to simpler equipment requirements [155,175,178] (Table 6). Additionally, wet milling is more suited to large-scale production, while dry milling is well suited for small-scale ethanol plants that require less equipment and investment [176], and it provides up to a 15% higher ethanol yield [179].

Table 6. Comparison of the wet- and dry-milling processes.

Comparative Elements	Wet Milling	Dry Milling	References
Ethanol yield	~29 kg from 100 kg corn	~34 kg from 100 kg corn	[179]
Investment cost	~USD 79.3 million	~USD 51.8 million USD	[160,180]
By-products	~5 kg corn gluten meal ~22 kg corn gluten feed ~3 kg corn germ oil, fiber, feed steep water, and CO_2	~32 kg distiller's dried grains with solubles (90% dry content) ~32 kg CO_2	[179]

One of the by-products derived from dry milling is known as distillers' dried grains with solubles (DDGS), which consists of the undigested portion of grains left after ethanol fermentation [181]. DDGS is commonly utilized as feed for livestock and poultry [181]. It boasts high fiber and protein contents, making it a valuable source of carbon and nitrogen for microbial fermentations [182].

Based on data from the American Renewable Energy Association (AREA), global fuel ethanol production reached an estimated 29.1 billion tons in 2019 [183]. The United States and Brazil were the leading contributors, comprising 54% and 30% of the worldwide production, respectively [183]. China also emerged as a noteworthy participant, ranking as the third-largest ethanol producer and contributing approximately 4.0% to the global ethanol production [183]. It is important to note that in the United States, the dry-milling process accounts for a significant majority, constituting 90.1% of ethanol production, while the wet-milling process represents only 9.1% [183].

6. Insights and Implications across the Main Generations of Biomass

The global shift towards sustainable energy sources and reduced carbon emissions has accelerated the exploration of alternative fuels, one of which is bioethanol.

Production of first-generation bioethanol from sugar-based feedstocks presents itself as a promising alternative to petroleum-based transportation fuels, offering reduced pollutant emissions compared to corn-based bioethanol [48]. Countries like Brazil and the U.S. have been pioneers in bioethanol production for over two decades [184]. For instance, Brazil has been utilizing commercial bioethanol production technology from sugarcane juice for two decades [185]. First-generation bioethanol production boasts advantages such as lower production costs, familiar feedstocks, and energy-efficient methods, resulting in reduced fossil fuel requirements along the biofuel value chain, ultimately mitigating greenhouse gas emissions [186].

However, concerns over the competition of first-generation bioethanol production with food resources have raised sustainability debates, particularly regarding the need for fertile soils with ample rainfall or irrigation for sugarcane cultivation [187]. Greater potential in bioethanol production lies in non-food lignocellulosic biomass, where significant amounts of bagasse and straw are produced during sugarcane juice processing for either bioethanol or sugar production [188]. In Brazil, bagasse is mainly used as fuel in boilers to meet the steam energy demand for first-generation bioethanol production or to generate electricity for the grid [189], which does not align with modern biorefinery concepts requiring efficient biomass resource utilization [190]. Sugarcane bagasse and straw, being lignocellulosic materials, can efficiently support the simultaneous production of second-generation bioethanol, bioelectricity, and heat [191,192]. Extensive research efforts have been made to develop viable technology for bioethanol production from lignocellulosic biomass [193]. However, the economic feasibility of large-scale second-generation production in standalone facilities remains a subject of debate [194].

Commercial second-generation bioethanol production from corn stover has already begun in Italy and the U.S., while demonstration plants for commercial-scale production are in progress in Sweden and Canada [194]. A significant challenge in second-generation bioethanol production is the pre-treatment stage, which accounts for 18% of production costs [195]. Other factors influencing second-generation bioethanol production include plant capital costs, feedstock costs, enzyme expenses, and energy requirements [196]. One proposed method to reduce second-generation production costs is by achieving high ethanol yield and concentration, possibly through an increase in water-insoluble solids [185], although this may lead to decreased yield due to inhibition from degradation products and reduced mass transfer [197]. Besides pre-treatment, another significant concern is the energy consumption during purification [198]. Achieving a minimum of 40 g/L or more of bioethanol concentration in a standalone second-generation process is often challenging, whereas fermentation broth from first-generation processes can yield bioethanol concentrations as high as 80 to 115 g/L [199]. Biological limitations in the second-generation process result in a more dilute ethanol product, increasing purification costs compared to the first-generation process [199].

For third generation, the growth rate of algae is 20 to 30 times faster than that of food crops, and they can yield up to 30 times more fuel compared to equivalent quantities of other biofuel sources [200]. But the primary barrier hindering the widespread adoption of algae stems from their high production costs and limited cost-effectiveness [200]. This is because the entire process of cultivating, harvesting, separating, and processing algae into final fuels comes with substantial expenses [198–201]. To illustrate, the cost of producing microalgae is approximately 5–7 times greater than that of lignocellulosic biomass [202]. Furthermore, the production of fuels derived from algae demands a significant initial capital investment [203,204]. It is worth noting that relying solely on biofuel production from algae is not likely to be financially sustainable, and other economic approaches will play a pivotal role in making this viable [26,205]. Determining the exact quantity of algae that can be sustainably grown, harvested, and processed remains somewhat uncertain [200,206]. For instance, it is common practice to use fossil fuels for various stages, including cultivation, collection, production, transportation, and distribution of algae-based biofuels [205,206].

7. Conclusions

In conclusion, this review delves into the potential and advantages of producing bioethanol from biomass feedstock as a sustainable alternative to fossil fuel-based energy. It primarily focuses on selecting first-generation feedstocks for bioethanol production, with a specific emphasis on employing the dry-milling process for corn. The discussion yields key takeaways, emphasizing the pivotal role of transitioning from fossil fuels to bioethanol in addressing environmental challenges tied to traditional energy sources. Bioethanol production, particularly from first-generation biomass feedstocks like corn, wheat, sugarcane, and cassava, offers benefits such as reduced greenhouse gas emissions, enhanced energy security, and decreased reliance on volatile petroleum markets. Opting for these feedstocks provides a practical starting point due to their established agricultural practices and infrastructure, facilitating large-scale production. The straightforward conversion processes associated with first-generation feedstocks make them economically and technologically viable options. Among bioethanol production methods, the dry-milling approach for corn stands out by demonstrating higher ethanol conversion efficiency and cost effectiveness compared to wet-milling processes. Dry milling not only maximizes ethanol output per ton of corn but also yields valuable co-products like DDGS feed, corn oil, and carbon dioxide, bolstering the economic viability of the ethanol industry. In summary, transitioning to bioethanol production from first-generation biomass feedstock, especially through the dry-milling process for corn, presents a promising avenue for a more sustainable and environmentally friendly energy future. While challenges such as optimizing efficiency and managing raw material costs persist, the undeniable benefits of bioethanol production propel us toward a cleaner, more sustainable energy landscape, reducing reliance on fossil fuels and mitigating climate change impacts.

Considering the future trajectory of emerging technologies, there is a growing consensus among experts that the coming years may witness a gradual shift towards second-, third-, and potentially fourth-generation biofuels. This transition is expected to bring about significant advancements in sustainability while reducing reliance on food crops and enhancing carbon capture capabilities. However, achieving this transition will require collaborative efforts from policymakers, researchers, and industry players to overcome current challenges and pave the way for a more sustainable energy landscape.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflicts of interest.

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