

Review

Lignocellulose Biofuels: Advanced Thermochemical and Catalytic Conversion Processes with Global Market Perspectives

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Abstract

The increasing global demand for sustainable energy solutions has intensified the need for efficient and environmentally friendly biomass-conversion technologies. Among these, thermochemical processes, such as pyrolysis, gasification, and hydrothermal liquefaction, have emerged as promising pathways for transforming lignocellulosic and other organic waste materials into valuable biofuels and biochemicals. This paper presents a comprehensive evaluation of advanced thermochemical conversion and catalytic conversion methods, focusing on their operational mechanisms, catalytic enhancements, and product yields. The efficiency, environmental impact, and economic feasibility of various thermochemical platforms, including recent developments in catalyst design and process-integration strategies, are compared, and innovative approaches to optimize hydrogen generation, improve carbon efficiency, and minimize undesirable byproducts through tailored reaction conditions and bifunctional catalytic systems are explored. Recent advances as well as the current challenges related to feedstock variability, process scalability, and system sustainability are highlighted. By identifying critical research gaps, this study provides strategic insights aimed at guiding future improvements in thermochemical biomass utilization for clean energy production within a circular economy framework.

Keywords: lignocellulosic biomass; thermochemical conversion; biofuel production; catalytic upgrading; hydrodeoxygenation; sustainable energy systems



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1. Introduction

Environmental protection has become a major public concern owing to numerous problems, the worst of which stem from climate change, due to excessive fossil fuel combustion which has changed the planet's carbon cycle [1]. The consequences of these changes include massive environmental impacts such as air contamination, climate variation, and global warming, which affect energy stability and global economic development [2]. In their Fourth Assessment Report, the Intergovernmental Panel on Climate Change stated that the rising worldwide population and energy demand per capita have caused a rapid increase in greenhouse gas (GHG) emissions, with the transportation sector experiencing the highest growth over the past 10 years [3]. The global energy needs of the transportation

and industrial sectors are met using oil. By 2030, the worldwide consumption of oil will increase from 84 million barrels per day to 116 million barrels per day, with transportation accounting for ~60% of this consumption [4]. Therefore, environmental problems act as driving forces for the use of energy and the induction of renewable energy using clean energy resources.

The 20th century laid the foundation for the evolution of the organic chemical manufacturing industry's dependence on oil refining, while the 21st century can be credited with the improvement of a modern organics industry dependent on biomass refining [5]. Currently, the emphasis is on biomass, as part of efforts to pursue alternative green resources that can contribute significantly to fulfilling society's energy needs in an environmentally friendly manner [6]. Bioenergy derived from lignocellulosic biomass (LCB) is a primary alternative energy source. LCB, a renewable resource, comprises various agricultural wastes. Although biofuels obtained from lignin, cellulose, and hemicellulose exhibit higher GHG emissions throughout their lifecycle than solar and wind energy, their emissions are still considerably lower than those of fossil fuels. Emissions from lignocellulosic biofuels are primarily derived from biomass cultivation, conversion, and processing [7]. Although biofuels are generally more sustainable than fossil fuels, they are more expensive than wind and solar energy. Solar photovoltaic and wind energy exhibit reduced lifecycle GHG emissions, primarily from the manufacturing and installation phases, rendering them more sustainable in the long term [8]. Researchers have reported that 30–70 g per kWh of carbon dioxide (CO₂) is emitted upon conversion of cellulosic biomass into ethanol, whereas solar and wind energy emit 20–60 g per kWh of CO₂, indicating that the latter remain sustainable models for controlled GHG emissions [9–11].

Despite the higher GHG emissions of biofuels than those of solar and wind energy, they are still essential for industries such as heavy transport and aviation, where electrification is difficult.

Liquid biofuels can benefit from the existing fuel-delivery systems for storage and transportation [12]. Various biorefinery processes and methods have been developed to sustain biofuels and compounds in biomass. The main obstacle is the development of crops having the required physical and chemical properties to increase biomass output by two- or three-fold [13]. Several methods for bioenergy engineering plants have been proposed as possible means for improving the economics of biorefineries [14] and targeting specific biomass characteristics to increase fuel efficiency by enhancing the hexose/pentose ratio of polysaccharides in cell walls, changing lignin properties, and reducing cell wall recalcitrance. Recent studies have focused on improving biomass production through high-value photosynthesis [15]. Doubling global productivity with this approach would rely on identifying fundamental productivity constraints and eliminating them through modern genomic instruments [16]. Although research and development in plant metabolic engineering is ongoing, no structural study has analyzed the effect of such engineered approaches on the manufacturing costs of biofuels and the minimum amount of production needed at a commercial scale [17–20].

Currently, most countries depend on traditional resources such as oil and coal for energy production, which contribute to air pollution and global warming [21]. Moreover, the remarkable population growth in the past few decades, as well as lifestyle transformation, are among the main factors responsible for the high consumption of energy worldwide, and the trajectory is anticipated to remain the same in the coming years [22].

Owing to the profusion of renewable biomass in nature, it has become a vital energy source in the world for replacing fossil fuels [23]. Biomass resources are considered organic materials because solar energy is converted into chemical energy. Most biomass resources are derived from different agricultural operations or as residues or products from the waste

of other operations in agriculture, industry, and forests [24]. These products are considered carbon neutral. Therefore, owing to the potential to derive different fuels from biomass, such as biodiesel, bioethanol, and biohydrogen, which can compete with fossil fuels in the global market, interest in biofuels is soaring [25].

Because biorefinery types and processes, biofuels and their types, biomass sources, and the chemical structures of biomass have already been thoroughly investigated, we did not cover these topics in this review. Instead, we focus on recent advancements in thermochemical conversion, catalytic conversion methods, and the use of supercritical fluids (SCFs) and ionic liquids (ILs) in biorefineries to enhance the yields and properties of the generated biofuels. Furthermore, we discuss the diverse applications of biofuels and their current markets to highlight their advantages and opportunities for boosting the economy and maintaining the environment. Researchers and scientists around the world are working to improve biofuel production and enhance their positive impact on the social, economic, and environmental aspects of daily life.

Although transesterification and esterification are catalytic rather than thermochemical processes, they are included in this review as they represent the industrial alternatives to thermochemical biofuels and share key catalytic design and feedstock economics with the thermochemical processes discussed in this review. Discussing and presenting them with pyrolysis, gasification, and liquefaction-based biofuels allow a direct comparison of yield, catalyst behavior, and market performance across both catalytic and thermochemical biofuel production processes.

Different existing reviews have addressed individual thermochemical conversion routes separately, such as focusing specifically on pyrolysis operating parameters and reactor design [26–28], on gasification technologies and hydrogen generation [29–31] or on hydrothermal liquefaction system design and biocrude upgradation [32–34]. Some reviews have analyzed catalytic deoxygenation mechanisms [35] and the downstream applications and market potential of bio-oil [36–38]. While these review papers are informative within their respective technical domains, they do not provide a comparative, cross-technology synthesis linking catalyst design, hydrogen and carbon-efficiency optimization, emerging solvent systems such as supercritical fluids and ionic liquids, and economic or market feasibility within a single integrated framework. The present review addresses this gap by (i) comparing pyrolysis, gasification, and hydrothermal liquefaction against common criteria of yield, catalytic enhancement, and environmental and economic performance; (ii) evaluating the underexplored roles of supercritical fluids and ionic liquids as green reaction solvents across these systems; and (iii) connecting process-level advances to bio-oil application markets and generation-based (first to fourth generation) biofuel comparisons. In doing so, this review moves beyond restating individual conversion routes and instead identifies bottlenecks common to all thermochemical platforms such as feedstock variability, catalyst deactivation, and scale-up economics, to provide comprehensive integrated research priorities rather than route-specific recommendations.

2. Overview of Biomass Conversion Technologies

LCB mainly refers to the carbohydrate polymers of cellulose ($C_6H_{10}O_5$)_n, hemicellulose ($C_5H_8O_4$)_n, and the aromatic polymer lignin ($[C_9H_{10}O_3(OCH_3)_{0.9-1.7}]_n$). An estimated 181.5 billion tons are produced annually, of which only 8.2 billion tons are used for various applications [39]. Lignocellulose can be transformed into numerous beneficial forms of fuel and valuable products, such as ethanol, methanol, biogas, pyrolysis oil, syngas, solid fuels, and bio-oil. It can also be transformed into electrical energy [40]. The feedstock category is determined by the characteristics of the biomass conversion technique [41]. In this review, we focus on thermochemical and physicochemical biomass-to-energy conversion

technologies as shown in Figure 1. The major processes for thermochemical transformations include torrefaction, combustion, pyrolysis, gasification, and liquefaction [42]. On the other hand, physicochemical transformation chiefly involves extraction with esterification and transesterification.

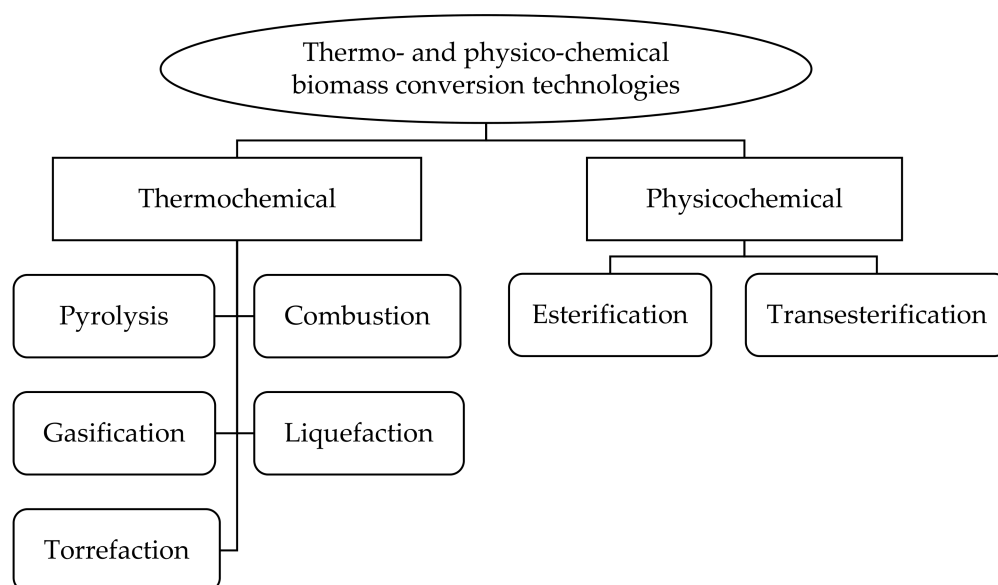


Figure 1. Thermochemical and physicochemical technologies for conversion of lignocellulosic biomass. This figure was reproduced from reference [43].

2.1. Thermochemical Conversion Technologies

Thermochemical techniques frequently involve the conversion of LCB at elevated temperatures and/or pressures, where the thermal decay of lignocellulose produces upgradable intermediates into value-added products. The primary thermochemical techniques include combustion, gasification, pyrolysis, torrefaction, and liquefaction [29]. Direct combustion involves firing biomass under oxygen to transform chemical energy into various types of valuable energy. The key distinction between combustion and pyrolysis is the presence or absence of oxygen during heating. Pyrolysis occurs without oxygen and yields bio-oil, biochar, or gases, depending on transformation parameters such as temperature, heating speed, contact time, reactor array, and feedstock type [26]. Liquefaction in the presence of a catalyst at elevated pressures and controlled reaction rates produces high-quality bio-oil. Pressures in the range of 1.0–20 MPa and temperatures in the range of 250–450 °C are typically used [27]. Gasification converts carbonaceous materials, such as charcoal, biomass, and bio-oil, into syngas. Torrefaction is a moderate pyrolysis procedure that thermally promotes the synthesis of hydrophobic, biodegradation-resistant, and homogeneous compounds [28].

2.1.1. Pyrolysis

Pyrolysis has gained considerable recognition because it allows the direct transformation of biomass into gaseous, liquid, and solid outputs by thermally decomposing the biomass without oxygen [44]. Pyrolysis is used to crack lignocellulose molecules into shorter molecules. Pre-pyrolysis, the first step, occurs between 120 and 200 °C and causes slight weight loss. Internal rearrangements such as bond breaking and the generation of free radicals and carbonyl groups occur during this step; therefore, trace amounts of H₂O, CO, and CO₂ are emitted. The second stage includes the main pyrolysis process, in which a substantial weight loss results from solid disintegration. The last stage of pyrolysis is the continual volatilization of char by additional splitting of the C–H and C–O bonds [45].

Numerous types of pyrolysis are available, such as fast, slow, flash, vacuum, and pressurized ultra-pyrolysis [46]. Two types of reactors are frequently used for pyrolysis: fixed bed and fluidized bed reactors. Pyrolysis is classified into four approaches based on the heating speed, use of catalysts, and/or heating path: (1) slow, (2) fast, (3) catalytic, and (4) microwave (MW) [47]. Slow pyrolysis takes place at a slow heating speed of 0.1–1.0 °C/s, at 300–700 °C, and with a contact time of 10–100 min. By contrast, fast pyrolysis is carried out at a heating speed of 10–200 °C/s at temperatures of 400–800 °C. On the other hand, flash pyrolysis is performed at a heating rate of more than 1000 °C/s, in a temperature range of 800–1000 °C. Finally, MW pyrolysis is typically performed at 500–800 °C and 500–2250 W [48], using an absorber content of 5–30 wt% [46].

In areas with abundant biomass, a pyrolysis biorefinery has the benefit of decentralized oil production, preserving the minerals in their origin and reducing the expense of transporting the resulting liquids. Through the economically efficient fractionation of pyrolysis oil, value-added materials can be created, producing different grades of oil required for promotion into fine chemicals, petrochemicals, automobile fuels, and energy. However, the rapid pyrolysis of bio-oils has some drawbacks, such as a high total acid number (TAN) (between 100 and 200), high oxygen concentration (about 40%), lower heating value, greater water quantity (~20%), and negligible solubility in crude oil and its fractions [27].

2.1.2. Gasification

Fuel production via biomass gasification began in the late '70s and the early '80s [39]. The process involves converting carbonaceous biomass into burnable gases such as methane, hydrogen, carbon monoxide, and carbon dioxide, in specified calorific amounts. Gasification is achieved by introducing a limited supply of oxygen (normally 35% of the amount required for the entire combustion) or an appropriate oxidant such as water or carbon dioxide [40]. Gasification also produces syngas, which is a mixture of carbon monoxide and hydrogen. The generated hydrogen can potentially be used as fuel in turbines and furnaces because it readily burns with air. The use of syngas as fuel results in high performance and decreases carbon emissions [41]. Moreover, gasification is rated as more ecologically benign than other options owing to the emission of less poisonous gases into the air and the use of solid side products [29]. Biomass gasification has numerous benefits, such as tight facility requirements, precise combustion control, and improved thermal efficiency [49]. Gasification has been found to have better material destruction, hydrogen yield, and energy yield than pyrolysis [30]. The slow commercialization of the gasification process is due to its economic disadvantages. A key issue is ash fouling, which can significantly reduce gasification efficiency and cause financial problems. Although various gas systems have been developed, high-performance systems have not yet been developed [31].

For third-generation biomass types, such as microalgae, the relevant gasification process is classified into two groups: (1) conventional gasification and (2) supercritical water gasification. Conventional gasification takes place at high temperatures of 800–1000 °C and low pressures of 1.0–10 bar, where the dried biomass interacts with an insufficient amount of oxidizer like water, steam, air, or oxygen [46]. This approach has been commercially exploited but suffers from inferior thermal productivity when undried biomass is used [50]. In supercritical water gasification, microalgae are directly converted to gaseous products under conditions above the water critical point (374 °C and 22.1 MPa), without drying [51].

2.1.3. Liquefaction

Hydrothermal liquefaction is the transformation of biomass into liquid hydrocarbons in the presence of water and catalysts [52]. In contrast to pyrolysis, which produces extremely oxygenated bio-oil, liquefaction generates bio-oils with less oxygenation, which

have a better heating value and improved fuel properties. However, liquefaction-derived bio-oil, also known as heavy oil, is a sticky liquid, similar to tar, and its viscous nature makes it difficult to handle. In the reaction system, oil is typically mixed with organic solvents (e.g., acetone, propanol, butanol, ethyl acetate, methyl ethyl ketone). These solvents have proven effective in forming heavy oils with low viscosities [32]. Hydrothermal liquefaction takes place in the temperature range of 280–370 °C and pressure range of 10–25 MPa [33], where water is the most appealing solvent for liquefaction owing to its abundance and low cost. Catalysts influence bio-oil yield and quality.

In general, catalytic liquefaction is a hydrothermal liquefaction process executed using an acidic catalyst (H_2SO_4 , HCl , or H_3PO_4) or an alkaline catalyst (Na_2CO_3 , $\text{Ca}(\text{OH})_2$, KOH , NaOH , or K_2CO_3). The use of a catalyst decreases the bio-oil content of oxygen and nitrogen, with a consequent increase in the heating value [34].

2.1.4. Torrefaction

Torrefaction, a thermochemical technique, is used to convert raw biomass into a coal-like substance with improved fuel quality. Torrefied biomass is more fragile, easier to crush, and less energy-intensive. Furthermore, torrefaction facilitates storage and minimizes the water uptake of the biological degradation product. Torrefaction occurs under anaerobic ambient pressure, in the temperature range of 200–300 °C, for 15–60 min [46]. It liberates humidity and other volatile compounds from the biomass with the concomitant thermal dissociation of lignin, hemicellulose, and cellulose to generate dry, solid, torrefied bio-coal or biomass. The overall treatment of biomass can be divided into four stages: storage, drying, torrefaction, grinding, and pelletization.

2.2. Transesterification and Chemical Conversion of Biomass

Physicochemical conversion, called mechanical extraction, is a process based on mechanical conversion for extracting oil from the seeds of different crops, such as rapeseed and flaxseed [53]. This procedure converts the extracted oil, a type of liquid fuel, into methyl esters of fatty acids, called biodiesel, via esterification. In addition, physicochemical conversion involves the transesterification of biodiesel. Furthermore, this procedure results in oils and solid cakes that are used for animal feed [54].

Esterification is a catalytic chemical process in which fats and oils obtained from biomass are transformed into esters and water. Transesterification converts triglycerides into esters of fatty acids (biodiesel) and glycerol, a co-product in some microalgae cells (third-generation biomass), using accumulated lipids [55]. Table 1 summarizes the conditions and products of thermochemical and physicochemical biomass-conversion technologies [43].

Transesterification of Biomass Using Microwave-Assisted Heating as a Green Chemistry Approach

MWs are a form of electromagnetic radiation with wavelengths ranging from 1.0 cm to 1.0 m and frequencies in the 300–300,000 MHz range [56]. MWs with a frequency of 2.45 GHz are specifically used for domestic purposes, so as not to interfere with telephone and satellite communications or other industrial applications [57]. In MW-assisted heating, three main mechanisms are involved: reorientation of the dipole, ionic conduction, and interfacial polarization [58]. MW-assisted heating is often used for biofuel synthesis from second-generation (biomass waste residues) and third-generation (microalgae) feedstocks [59].

Table 1. The operating conditions, products, and comparative advantages and limitations of thermochemical and physicochemical biomass-conversion technologies.

Process	Temperature (°C) & Heating Rate	Pressure/ Atmosphere	Reaction Time	Major Products	Mode of Heating	Key Advantages	Key Limitations
Direct combustion	1200–1300	Oxygen rich	5–10 min	Heat/power	Contact	Simple, low cost, suitable for diverse feedstocks (including wet), mature technology	Low thermodynamic efficiency, generation of harmful contaminants, loss of valuable chemical byproducts, constrained by high moisture and ash contents
Slow pyrolysis	300–700, 0.1–1.0 °C/s	Oxygen free	10–100 min	Biochar (high yield)		Simple, low-cost, high solid yield	Long residence time (10–100 min)
Fast pyrolysis	400–800, 10–200 °C/s	Oxygen free	0.5–5 s	Bio-oil		High liquid yield	High oxygen content (approximately 40%), unstable oil
Flash pyrolysis	800–1000, >1000 °C/s	Oxygen free	5 s	Bio-oil/biogas		Rapid conversion	High capital cost, difficult to control
MW assisted pyrolysis	500–800, Power 500–2250 W	Oxygen free	6–25 min	Bio-oil/bio char	Non-contact	Volumetric uniform heat	Needs MW absorber materials (biomass is a poor absorber)
Hydrothermal Liquefaction	250–4000	10–25 MPa		Bio-crude with low O ₂	Indirect heating	Ease in handling wet biomass, better heating value than pyrolysis	Tar production, high viscosity of the final products, catalyst required
Conventional Gasification	800–1000	Limited O ₂ /steam, 0.1–1 MPa		Syngas	Superficial heating	Higher energy yield than pyrolysis, Higher H ₂	Dry biomass feedstock required, Ash fouling
Supercritical Water Gasification	>374	>22.1 MPa	---	Syngas		Drying is not required, suitable for wet feedstocks	High pressure required
Torrefaction	200–300	Anerobic, ambient pressure	15–60 min	Torrefied biomass/char/ash		Hydrophobic final product, better storage and handling	Only a pre-treatment process, does not produce fuel as end product
Esterification Trans-esterification	25–60	Ambient	Variable	Biodiesel/glycerol	Non-contact/ Volumetric	High selectivity, mild conditions, high process control	Lower product yield than thermochemical processes, feedstock (oil/lipid) dependent

Biodiesel is a fatty acid methyl ester (FAME) often synthesized by the reaction of methanol with fats and oils derived from biomass and other wastes [60]. Many methods have been developed for biodiesel production. In this process, commonly termed transesterification, the desired product is obtained in the absence or presence of a catalyst such as an acid [61], enzyme [62], base [60], or metal oxide [62]. The MW energy and reaction time play an essential role in biodiesel production by transesterification [63]. Recently, MW-assisted transesterification has been favored owing to its notable advantages over traditional heating, such as faster rates of chemical reaction and lower energy consumption [64]. The modern trend in biodiesel production research has been MW-assisted catalytic transesterification, where higher FAME yields have been attained with a lower MW power and shorter reaction time [59].

Table 1 compares MW-assisted and conventional heating methods to determine the advantages of MWs based on five parameters: energy consumption, reaction time, ease of operation, product, and mode of heating [59]. MWs can penetrate deeply and thus have better internal heat generation, provided that the catalyst and solvent are good MW absorbers, as biomass is a poor MW absorber. MW-assisted heating results in high yields and desirable product properties owing to better heat transfer. MW heating can be quickly switched on and off, or the power and time can be preset based on the material mass or volume, allowing for a high level of control. According to a literature review, a higher yield and enhanced properties of the final product can be achieved using MW heating owing to the effective heating rate within a short period. MW can perforate the container wall and biomass species owing to noncontact heating, whereas conventional heating leads to heat and energy dissipation owing to conduction and convection phenomena. MWs uniformly heat the material owing to volumetric heating, whereas conventional methods heat the surface owing to superficial heating [59].

Gupta and Rathod [65] performed an MW-assisted catalytic transesterification of waste cooking oil (WCO) with a catalyst weight loading of 1.03% (*w/w* of WCO). With an optimum methanol-to-WCO molar ratio of 7.46:1, at 62 °C for 15 min, the maximum theoretical (calculated using Design Expert 7.0 software) and experimental yields of biodiesel were 95.46% and 94.86%, respectively—double that of the traditional method. Ali et al. [66] found that the price of traditional transesterification with the maximum FAME yield of 86% could be reduced via the MW-assisted catalytic transesterification of WCO using 0.782 g of lipase at 44.2 °C for 24 h. Thirugnanasambandham et al. [67] achieved a 97% yield of bio-oil via MW-assisted catalytic transesterification of WCO at 70 °C, 325 W, and 3.30 min, with a catalyst loading of 1.0 g/g oil.

An MW-assisted catalytic process was used for the transesterification of papaya, jatropha, and olive oils under reaction conditions of 3.30 min at 700 W, where the critical factors were found to be the methanol-to-oil ratio and temperature [68]. Furthermore, Chang et al. [69] transformed a mixture of jatropha and castor oil (1:1 molar ratio) and a mixture of oil and methanol (1:12 molar ratio) into a 95% yield of methyl esters over magnetite-supported calcium hydroxide (7Ca:1Fe molar ratio). Their catalysts are stable, recyclable, and reusable owing to their ease of separation. Dehghan et al. [70] performed MW-assisted catalytic transesterification of olive oil in 9 min at 500 W to enhance methyl ester yields, where the yield of methyl ester was found to be a function of the catalyst quantity, reaction time, power level, and methanol/oil ratio.

Devasan et al. [71] reported a novel porous sulfonic acid-functionalized banana peel catalyst for biodiesel production using oleic acid as a model substrate and MW irradiation. Adopting a response surface methodology (RSM) and central composite design approach, they achieved a notable biodiesel yield of $97.9\% \pm 0.7\%$ under optimized reaction conditions, which included a methanol-to-OA molar ratio of 20:1, a temperature of 80 °C, and a

catalyst loading of 8 wt% for a duration of 55 min. The catalyst demonstrated remarkable stability during multiple reuse cycles, with a minimum of five recycling and minimal loss of activity. This approach resulted in a substantial biodiesel yield, demonstrating the efficacy of integrating biowaste-derived catalysts with MW heating for sustainable biodiesel generation.

Yadav et al. [72] used a functionalized heterogeneous catalyst synthesized from lignin-rich biomass, specifically walnut shell powder (WNS), in a low-temperature hydrothermal carbonization process to produce sulfonated carbon (WNS-SO₃H). This catalyst efficiently transformed oleic acid into methyl oleate through an MW-assisted esterification reaction. Under optimized conditions (9 wt% catalyst loading, 1:16 oleic acid-to-methanol molar ratio, 60 min reaction time, and 85 °C temperature), the conversion of oleic acid to biodiesel was determined to be 99.01% ± 0.3%. These results indicate that the use of waste walnut shells addresses environmental issues and contributes to sustainable energy solutions. The WNS-SO₃H catalyst is suitable for the sustainable, environmentally friendly, and cost-effective production of biodiesel through the esterification of oleic acid. Furthermore, the significant volume of walnut shell waste and enhanced reusability of the catalyst render it suitable for large-scale production.

3. Catalytic Conversion of Lignocellulose-Based Biomass

Several valuable aliphatic and aromatic compounds and biofuels can be produced by the catalytic cracking of LCB through catalytic pyrolysis, liquefaction, gasification, hydrolysis, deoxygenation, hydrogenation, and dehydrogenation reactions over monofunctional, bifunctional, or multifunctional catalysts [73]. Bifunctional catalysts are more widely used than monofunctional catalysts [74] to produce valuable compounds including diverse fuels such as hydrogen, methane, and ethanol, and chemicals such as fructose, glucose, sorbitol, lactic acid, and levulinic acid [75].

3.1. Bifunctional Catalysis

Bifunctional catalysis can separately activate both nucleophilic and electrophilic substrates over the distinct active sites of a single catalyst [76]. Thus, such catalysts possess two different active sites and can synchronously promote the two categories of reactions. Bimetallic catalysts and metal–metal oxide catalyst systems catalytically control the transformation of biomass reactions by enhancing the reaction rate and product selectivity, decreasing the consumed energy and improving productivity [77,78]. Heterogeneous bimetallic catalysts are grouped into three categories based on the metals involved: noble metals (e.g., Pd–Au, Au–Ru), a noble metal paired with a non-noble metal (e.g., Pt–Cu, Pd–Fe), and non-noble metals (e.g., Ni–Co, Fe–Co) [79]. The catalyst was loaded onto a monolith to reduce the pressure drop over the catalyst; the monolith is composed of many parallel tracks through which gaseous reactants can readily pass with a minor pressure drop, as depicted in Figure 2. Monoliths can be formed from either ceramic material such as cordierite or metallic materials such as FeCr alloy steel [80]. Recently, metallic materials have been given more consideration owing to their high thermal conductivity and potential for more sophisticated coating designs [81].

The choice between noble metals (Pd, Pt, Ru) and non-noble metals (Ni, Fe, Co, Cu) bimetallic systems also carries direct economic implications for large-scale applications. Non-noble metal combinations such as Fe–Ni and Ni–Co are increasingly used for industrial-scale catalytic processes owing to their availability, cheapness, and greener relative to noble metals, which often are superior in initial activity and selectivity [82]. This cost/performance trade-off is a central idea for translating lab-scale bifunctional catalyst results into commercially viable biorefinery operations.

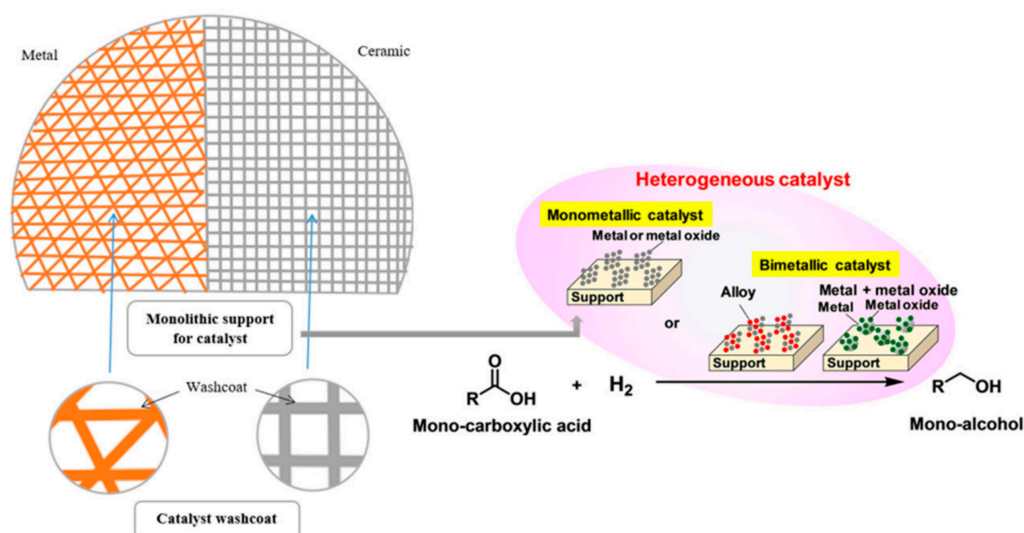


Figure 2. Schematic representation of monometallic and bimetallic catalysts and their supporting materials [81]. Figure reproduced with permission from Wiley.

Bimetallic oxide catalysts are advantageous owing to their catalytic activities, selectivities, thermal and chemical stabilities, and synergistic effects. These catalysts improve the efficiencies of reactions such as hydrolysis and hydrogenation, particularly Ni–Cu [83] and Co–Mo, and demonstrate enhanced biomass-conversion performance [84]. Ensuring the stability of the desired crystallographic phase at elevated temperatures and in chemically reactive surroundings is essential for maintaining long-term catalytic effectiveness. Ni–Co catalysts are more stable than their monometallic counterparts owing to stabilizing interactions and are more efficient in specific biomass-conversion processes owing to the synergistic electronic and geometric effects of the two metals, which enhance the catalytic performance [83,84].

Among metal-based catalysts, bimetallic catalysts are widely used in biomass conversion. Generally, the addition of two metals helps modify the efficiency of the main metal [35]. Several studies have investigated the role and mechanisms of the second metal state in improving the efficacy, selectivity, and rate of the reaction [85]. For example, using a Pd/Au catalyst, it was found that oxygen molecules degraded over the Pd catalyst, whereas CO was oxidized on the Au catalyst [86]. In the metal–metal oxide catalyst mechanism, which is illustrated on Pt/ZrO₂ for the dry reforming of methane, Pt metal activated and dehydrogenated methane to form CH_x species, whereas the interface sites in Pt/ZrO₂ were capable of dissociating carbon dioxide. By contrast, *m*-cresol preferentially followed the pathway of ring hydrogenation for oxygen removal over PtMo/Al₂O₃. By doping the catalyst with an oxophilic modifier, tautomerization was possible, resulting in a keto intermediate that dehydrated into toluene [86].

Beyond activity and selectivity, the second metal in a bimetallic system also plays an important role in suppressing coke-based deactivation. For instance, incorporating both Fe and Ni into a ZSM-5 catalyst increased coke resistance relative to the corresponding metallic Fe/ZSM-5 or Ni/ZSM-5 during catalytic pyrolysis of sawdust, although catalytic activity still declined progressively with increasing cumulative biomass-to-catalyst ratio [82]. This behavior illustrates that bimetallic design can extend catalyst lifetime without fully eliminating deactivation which is further discussed in Section 3.4.

Bifunctional catalysts based on metal–metal oxide systems are efficient for the dehydrogenation/hydrogenation of biomass materials to produce new valuable products, such as alkenes [87]. The acidic sites of the catalyst protect the alkenes and convert them into carbonium ions [88]. Zeolites are acidic catalysts that can support metal catalysts.

In this context, Liang et al. synthesized Ni catalysts with several supports (kieselguhr, bentonite, ZSM-5, SiO₂, Al₂O₃, and TiO₂) for the hydrogenation/dehydrogenation of cellobiose and glucose and found that the bifunctional nickel catalyst played a critical role in controlling hexitol selectivity [89]. Zhongzh et al. studied the selective dehydrogenation/hydrogenation of N-heterocycles using a bifunctional catalytic system. The type of support, its interaction with the metal, bimetallic effects, electronic structure of the active metal, core-shell structure, and nanoparticle size have all been shown to affect the catalytic performance [90]. In another study, various oxides (Al₂O₃, TiO₂, SiO₂, ZrO₂, and CeO₂) were employed as supports for copper metal nanoparticles, with average sizes of 2.2–2.8 nm, for the dehydrogenation of 2-butanol, demonstrating that a bifunctional catalyst could be used as an alternative route for hydrogenation to generate valuable products, while an Au-supported catalyst hydrogenated furfural to furfuryl alcohol [91].

Recently, the potential for cost-effective hydrogen storage based on metal-catalyzed hydrogenation and dehydrogenation of quinoline was demonstrated, as shown in Figure 3 [90,92]. Several studies have investigated the possibility of storing hydrogen inside organic compounds to facilitate their transport and reuse. For example, Li et al. hydrogenated biomass derived from furfural to tetrahydrofurfuryl alcohol over several bifunctional catalysts using metal-metal oxide systems [93].

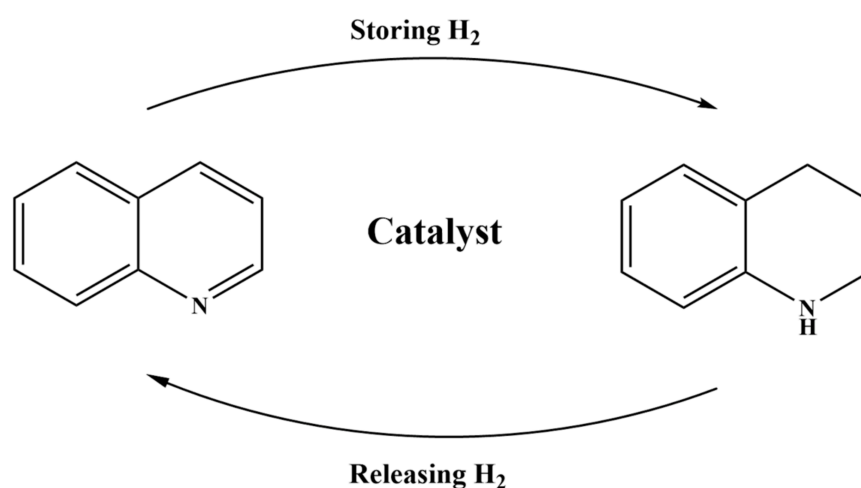


Figure 3. Hydrogenation and subsequent dehydrogenation of quinoline using a heterogeneous bifunctional catalyst.

3.2. Importance of Bifunctional Catalysts for Biomass Deoxygenation

Bifunctional substances have been studied extensively owing to their potential for use as oxygen-removal catalysts. In particular, the conversion of LCB compounds by pyrolysis requires novel catalysts for the selective removal of oxygen from the produced oil [74], as illustrated in Table 2 [86]. Generally, deoxygenation is important for obtaining hydrocarbons with added value [74]. Many compounds have been reduced using dual-functional catalysts. For example, selective oxygen removal and ring opening of substrates containing eight or nine carbons derived from 5-hydroxymethylfurfural [94] or furfural have been accomplished using bifunctional catalysts made of ruthenium nanoparticles [95], and alcohols, phenols, aldehydes, and ketones have been reduced into their corresponding alkanes [86].

Table 2. Selectivity and reaction conditions for oxygen removal of *m*-cresol or guaiacol over different bifunctional catalysts. The compiled data are drawn from the primary studies reviewed in [86].

Catalyst	Temp. (K)	P (atm)	PH ₂ (atm)	Met. Wt%	Reactant	Con. (%)	% Deox.	Ref.
Pt/Al ₂ O ₃	533	1	0.5	0.5	<i>m</i> -cresol	9.3	79.2 *	[96]
Pt/Al ₂ O ₃	533	1	0.5	1	<i>m</i> -cresol	18	82.6 *	
Pt/Al ₂ O ₃	533	1	0.5	1.7	<i>m</i> -cresol	38.3	80.5 *	
Pt/SiO ₂	533	1	0.5	1.6	<i>m</i> -cresol	54.9	82.1 *	
Pt/Al ₂ O ₃	533	1	0.5	1.7	<i>m</i> -cresol	30	76.1 *	[97]
Pt/TiO ₂	573	1	1	1	<i>m</i> -cresol	17	97 *	[98]
Pt/ZrO ₂	573	1	1	1	<i>m</i> -cresol	12	88.5 *	
Ni/SiO ₂	523	1	1	5	<i>m</i> -cresol	55.8	7.2 ^r	[99]
Ni/C	623	39.5	37.6	5	guaiacol	30.7	17.5 ^r	[100]
Ni/SiO ₂	573	1	1	5	<i>m</i> -cresol	16.2	14.2 *	[101]
Pd/C	573	1	0.4	5	<i>m</i> -cresol	10	78 *	[102]
Pd/SiO ₂	523	1	1	1	<i>m</i> -cresol	54.9	24.1 ^r	[99]
Pd/C	623	39.5	37.6	1	guaiacol	15.5	32.3 ^r	[100]
Fe/SiO ₂	573	1	1	5	<i>m</i> -cresol	8.8	60.2 *	[101]
Fe/SiO ₂	623	1	0.9	Not Rep.	guaiacol	50	37 ^r	[103]
Ru/SiO ₂	573	1	1	9.4	<i>m</i> -cresol	4.5	38.5 ^r	[104]
Ru/C	623	39.5	37.6	1	guaiacol	34.2	39.6 ^r	[100]

* Based on hydrocarbon selectivity%. ^r Based on product distribution%.

Table 2 also reveals a broader trend beyond catalyst-by-catalyst conversion and deoxygenation values: the acid-base character predicts which deoxygenation pathway dominates. Basic catalysts such as MgO and Na₂O/γ-Al₂O₃ favor oxygen removal via decarboxylation, whereas solid acid catalysts such as zeolites primarily promote decarbonylation and dehydration [105]. This feature is important to consider as decarboxylation and decarbonylation both remove oxygen as CO₂ or CO at the cost of carbon yield, whereas dehydration retains more carbon in the liquid product but removes oxygen only as water. The catalyst selection should not be based only on overall deoxygenation efficiency but also on which pathway best preserves carbon yield for the intended fuel application.

3.3. Emerging Catalyst Systems

Beyond conventional bimetallic and metal–metal oxide catalysts, several emerging catalyst classes are gaining attention for lignocellulosic biomass conversion. Single-atom catalysts (SACs), which disperse isolated metal atoms to maximize atomic utilization, have demonstrated high activity, selectivity, and stability in catalytic systems. For example, ruthenium-based SACs prepared from a metal–organic framework (MOF) precursor showed strong performance in the reductive upgrading of levulinic acid to γ-valerolactone, which is a biomass-derived chemical [106]. Because SACs use 100% atomic utilization, they offer a route to reducing the loading of costly noble metals while maintaining the same level of catalytic performance. MOF-derived catalysts have growing research interest because their tunable pore structure and metal-node chemistry allow precise control over active-site geometry. However, their long-term hydrothermal and thermal stability under realistic biomass conversion conditions remains an open question.

3.4. Catalyst Deactivation and Regeneration

Despite the demonstrated performance of bifunctional, bimetallic, and metal–metal oxide catalysts described above, catalyst poisoning and subsequent deactivation remain the primary barrier to their industrial applications. In hydrodeoxygenation (HDO) and catalytic pyrolysis, this poisoning occurs mainly through three mechanisms: carbonaceous deposition (coking), sintering of active metal particles, and poisoning of active sites, particularly by nitrogen, sulfur, and phosphorus compounds and water present in biomass feedstocks [107]. All these issues lead to a reduction in the effective catalytic surface area, a change in surface chemistry, and a conversion and selectivity decline over repeated use.

The severity and reversibility of poisoning and deactivation vary by catalyst system used. For the bimetallic Fe–Ni/ZSM-5 catalyst discussed in Section 3.3, deoxygenation activity declined steadily with increasing cumulative biomass-to-catalyst ratio, and regeneration by coke combustion restored much of the catalytic activity but resulted in partial, irreversible loss of acidic sites and pore structure [82]. On the other hand, some noble-metal HDO catalysts can show much greater durability such as Pt/TiO₂, which demonstrated stable performance over 100 or more reaction/regeneration cycles using wood biomass feedstock under near-atmospheric pressure conditions. However, its performance with lower-cost, higher-ash feedstocks remains less explored [105]. These catalysts indicate that durability should be the primary criterion in catalyst selection for thermochemical biorefineries rather than only initial activity. In addition, the regeneration protocols must be evaluated for their effect on long-term structural integrity rather than only short-term activity recovery.

3.5. Emerging Catalytic Approaches Beyond Conventional Systems

Besides the thermally driven bifunctional, bimetallic, and metal–metal oxide catalysts discussed above, various fundamentally different catalytic strategies are being explored at the lab scale for lignocellulosic biomass valorization, offering advantages in energy input, selectivity, and operating conditions.

3.5.1. Photocatalysis

Semiconductor photocatalysts including TiO₂, ZnO, g-C₃N₄, and graphene oxide composites can drive lignocellulosic conversion using solar or artificial light under near-ambient conditions via cleaving the structural linkages (C_β—O and C_α—C_β bonds in lignin) to recover fuels and value-added chemicals [108]. Photocatalytic processes can operate at ambient temperature and pressure. The main barriers in implementation are inefficient light absorption, rapid charge-carrier recombination, and issues with the engineering of photocatalysts. None of these approaches currently matches the efficiency or technological maturity of conventional thermochemical catalysis. However, photocatalytic approaches address specific limitations of conventional catalytic systems. The current work on photocatalysis remains largely confined to the lab scale.

3.5.2. Electrocatalysis

Electrocatalytic oxidation and reduction pathways provide an alternative route for lignocellulosic conversions by using electric energy for selective bond cleavage. Thermal catalysis provides high conversion but requires high energy input and causes coking, while electrocatalytic and photocatalytic processes operate under mild conditions with better selectivity, though scalability is limited by feedstock problems and electrode/catalyst challenges [109].

3.5.3. Plasma Catalysis

Non-thermal plasma combined with a metallic catalyst has shown great potential for upgradation of biomass syngas and removal of tar compounds. Mei et al. [110] used a Ni/ γ -Al₂O₃ honeycomb catalyst that was integrated into a gliding arc discharge plasma reactor and achieved 86.3% conversion of toluene and 75.5% conversion of naphthalene, together with H₂ and CO yields of 35.0% and 49.1%, respectively. This approach helped suppress undesirable byproduct formation compared to plasma treatment alone. This hybrid plasma-catalytic approach shows how coupling non-equilibrium plasma chemistry with conventional catalytic materials can address long-standing downstream challenges, including tar contamination in syngas, which are difficult to resolve using thermal catalysis.

4. Supercritical Fluids in Biorefineries

SCFs exist in a state beyond their critical point, where the temperature and pressure exceed their critical values. SCFs are versatile and sustainable for various applications. Their unique properties, including high density, low viscosity, and tunable solvency, make them attractive materials for food processing, pharmaceuticals, and environmental remediation.

One of the primary goals of biorefineries is the production of sugar and bioethanol. This strategy ignores other functional biomass molecules, which are viable alternatives to high-value chemicals, such as lignin and polyphenols. To circumvent this problem, an advanced integrated biorefinery method, which promotes valorization of all biomass streams for high-value products, can be used [111].

4.1. Use of Supercritical Fluids in Grape Seed Processing

When grapes are processed into wine and juice, the primary byproduct is grape seeds. Globally, more than 3 million tons of grape seeds are discarded annually [112]. The extraction of phenolic chemicals and oils from grape seeds has attracted considerable attention over the last few decades [113]. Grape seed oil is rich in unsaturated fatty acids such as linoleic acid and has a high tannin content, making it more resistant to peroxidation [114]. Phenolic chemicals found in grape seeds are also valued, and their extracts have been the focus of extensive research owing to their possible benefits for human health, including antioxidant activity [115]. Defatted seeds are considered residues of oil extraction and can be burned to provide energy. However, this residue still contains a considerable amount of valuable materials, such as carbohydrates and a high concentration of polyaromatics (lignin and other polyphenols). Therefore, recovering and using the residual fractions through additional exploitation may be more efficient than recovering energy from them. Adamovic et al. hydrolyzed grape seeds in supercritical water and successfully recovered liquid-phase sugar in yields reaching 61% within 0.27 s. A solid enriched with polyaromatics was produced [116]. Another SCL was used to extract oil from grape seeds. Supercritical CO₂ combined with pulsed electric fields resulted in higher oil yields (up to 81.8 ± 1.0 g/kg) than cold pressing (67.1 ± 0.2 g/kg). Extraction selectivity was improved, particularly for sterols and nonflavonoids (phenolic acids and trans-resveratrol), which sustained the oil quality in comparison with conventional cold pressing [117].

4.2. Use of Supercritical Fluids in Coffee Production

After water, coffee is one of the most consumed beverages worldwide, and the second most traded item after petroleum. According to the International Coffee Organization, coffee bean production reached 10.4 M tons in 2023–2024, an increase of 4.2% compared with the previous year. Many processing steps are required to obtain beverages from coffee beans, leading to the production of different byproducts. Furthermore, these byproducts contain

compounds such as caffeine, tannins, and polyphenols, which can be environmentally unfriendly [118]. After harvesting coffee cherries, the three primary phases required to obtain the beverage are as follows: (1) drying or wet processes, (2) roasting process, and (3) brewing process. The expected byproducts of these processes are coffee husk, pulp, silverskin, and spent coffee grounds [119]. Spent coffee grounds have been extracted using supercritical CO₂ to produce value-added materials. Three factors (temperature, pressure, and co-solvent) were optimized for the best results, leading to 11.97% (g_{oil}/100 g_{SCG}) oil enriched with diterpenes such as kahweol, cafestol, and 16-O-methylcafestol. Under optimal conditions, the diterpene concentration was increased by 212–410% at the cost of reducing the extraction yield between 39% and 79% compared with the conventional method involving n-hexane extraction [120].

5. Ionic Liquids in Biorefineries

ILs are organic salts composed exclusively of ions in the liquid state near room temperature. They have gained significant attention over the years owing to their unique properties such as low volatility, high thermal stability, and the ability to dissolve a wide range of polar and nonpolar materials. Therefore, ILs are useful solvents for many chemical reactions, including separation, catalysis, and electrochemistry, and are used in biorefinery systems to extract and process the most critical components of biomass, such as carbohydrates and lignin.

ILs have been used in many biorefinery applications, such as the pretreatment of duckweed biomass. Hallett et al. thoroughly investigated two ILs, dimethylethanolammonium formate ([DMEtA][HCOO]) and *N,N*-dimethylbutylammonium hydrogen sulfate ([DMBA][HSO₄]), for their potential benefits in the pretreatment of two duckweed species (*Spirodela polyrhiza* and *Lemna minor*). Their study focused on starch and protein recovery, sugar release, and metal extraction capabilities. [DMEtA][HCOO] illustrated excellent starch recoveries at 120 °C, whereas [DMBA][HSO₄] demonstrated comparable results at 90 °C. After 8 h of hydrolysis, most pulps had over 90% saccharification yields, exceeding those of “conventional” LCBs such as miscanthus or sugarcane bagasse. Almost half of the protein was soluble in [DMEtA][HCOO], and almost 80% was soluble in [DMBA][HSO₄]. The remaining protein is divided into pulp and lignin [120]. ILs have also been investigated for the extraction of natural antioxidants and therapeutics, such as carotenoids, from microalgae. ILs can enhance process efficiency and decrease the reliance on petroleum-based chemicals in the food industry. Tetrabutylphosphonium hydroxide can selectively extract 2.26 mg.g^{−1} dry cell weight (DCW) of lutein from the wet biomass of *Chlorella saccharophila* (*C. saccharophila*). By contrast, methanol extracts 0.10 mg.g^{−1} DCW of lutein in room-temperature-based extraction. Once again, the extraction was enhanced using RSM optimal extraction conditions. At 60 and 90 °C, lutein was three times more stable in IL than in methanol, the traditional solvent. Therefore, tetrabutylphosphonium hydroxide may eventually replace traditional organic solvents in the downstream processing of bioactive microalgal chemicals [121].

Beyond pretreatment and extraction applications, various research studies have analyzed the recovery and reuse of ILs, which are the central part of economic and environmental viability. Imidazolium-based ILs such as 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) were among the first shown to dissolve significant fractions of cellulose, with the dissolved cellulose subsequently regenerated/converted in amorphous form using anti-solvents such as water. This feature demonstrates an early proof of concept for solvent recovery alongside biomass conversion. Following this, 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]) has been used to achieve complete dissolution and partial delignification of wood with the ability to recover solvent [36].

Low-cost protic ILs synthesized from combinations of aqueous acid and amine base have been used in the Ionosolv pretreatment process, in which lignin is precipitated from the IL with the addition of water and the ionic liquid, allowing the solvent to be reused across multiple pretreatment cycles. Pretreatment cycles simplify solvent recovery and reduce both capital investment and solvent-vapor exposure [122].

Recent research studies have further analyzed IL recovery strategies by identifying anti-solvent precipitation, membrane separation, and distillation as the principal recycling techniques. In these processes, recovery efficiency is governed by the specific anion-cation pairing and its interaction with dissolved biomass components. Anions such as acetate and chloride are particularly known for disrupting the hydrogen-bonding networks within cellulose and lignin, affecting not only initial dissolution efficiency but also how readily the IL can be recovered and reused without any structural degradation [123]. IL-based pretreatments have shown the enhancement of downstream bioconversion efficiency across a wide range of feedstocks, positioning IL recyclability as a critical factor determining the economic competitiveness of IL-based biorefinery processes [124].

6. Applications of Bio-Oil

Bio-oil and bio-crude are produced using two main thermochemical methods, pyrolysis and liquefaction, and have primary applications in heat and energy boilers, power generation by diesel engines or gas turbines, and fuel transportation for diesel engines [37]. Three biomass-derived feedstocks, namely, sugars, lignocellulosic feedstocks, and triglyceride feedstocks, are used [125]. For cellulosic biomass, the most common high-yield and relatively low-cost method of conversion into bio-oil is rapid pyrolysis [126]. For lignocellulosic feedstocks, two different pathways can be used to produce many liquid biofuels: thermochemical conversion and hydrolysis, or biochemical/biotechnological and thermochemical transformation procedures [38]. Thermochemical conversion processes include gasification, pyrolysis, liquefaction, or hydrolysis [127]. Bio-oil has been evaluated as a fuel for electricity and heat generation in boilers, furnaces, diesel engines, and gas turbines and is used as a raw material in the production of synthetic gas and vehicle fuel. Nonetheless, this application necessitates amending a few of its undesirable properties, which primarily arise from its high oxygen content. Bio-oil is a source of a variety of valuable acidic compounds [128].

6.1. Potential Applications of Pyrolysis Bio-Oil as Replacement for Diesel and Petroleum Fuel

One advantage of bio-oil over fossil fuels is that it can be produced from a wide variety of sources. However, bio-oil cannot be applied as a transport fuel owing to its high viscosity, high water and ash contents, low heating value, volatility, and propensity for corrosion [129]. Instead, bio-oils can replace fossil fuels to supply heat, electricity, and chemicals [130].

Continuous research investigating biomass as an alternative for generating power using agricultural and forest residues is underway. Five types of biofuels are currently produced from palm oil biomass: hydrogen gas, bio-methanol, bioethanol, bio-briquettes, and pyrolysis oils. Slow pyrolysis-derived bio-oils are suitable fuels for industrial combustion. For example, palm oil is used in diesel engines, either directly or when converted into methyl esters [131]. As high-density oxygenated liquids, bio-oils are good replacements for liquid fossil fuels in boilers, diesel engines, and turbines [132,133]. Fast pyrolysis-derived bio-oils are a chemical feedstock for manufacturing chemicals and resins, such as fertilizers and acids, and adhesives, such as asphalt bio-binders [134].

Bio-oil is suitable as a replacement for diesel or fuel oil for generating electricity in numerous industrial applications such as boilers, heat-generating furnaces, diesel engines,

and gas turbines. In this context, bio-oil has been investigated as a fuel in both small- and large-scale systems for generating heat and power, where combustion devices include spray, combustion, and emission components [135]. Table 3 compares the reported performance and key operational challenges of bio-oil combustion across boiler, furnace, diesel engine, and gas turbine applications, discussed in detail in the following subsections.

Table 3. Comparative performance of bio-oil combustion applications in boilers, furnaces, diesel engines, and gas turbines.

Application	Scale/Example	Key Finding	Main Challenges	References
Boiler (Neste Oyj)	2.5 MW, dual-fuel burner	Stable operation at varying fuel oil and bio-oil ratios	High particulate emissions (2.5–5 Bacharach, ASTM D-2156)	[136,137]
Furnace (Oilon Oy/VTT)	8 MWth nominal, 4 MWth capacity	Lower emissions than heavy fuel oil except particulates	Longer flame, needs auxiliary fuel at startup	[138,139]
Diesel engine	Ricardo engine, 450 mL, 19.8–2400 rpm	Thermal efficiency similar to diesel	Corrosiveness, coking, ignition delay	[137,140,141]
Gas turbine	Orenda, 2.5 MWe	Lower SO ₂ /NO _x than diesel over full cycle	Higher particulates than diesel	[142]
Co-firing	Manitowoc, WI (coal + Red Arrow bio-oil)	Commercially demonstrated at scale	Storage, pumping, filtration handling issues	[142,143]

6.1.1. Combustion in Burner/Furnace and Burner/Boiler Systems

Devices that are widely used for generating heat and power are furnaces and boilers, which are typically less efficient than engines and turbines. However, they may work with a wide range of fuels, including fossil gas, naphtha, wood dust, and coal/water slurries [143].

The Red Arrow Products pyrolysis plant in Wisconsin, USA, is globally unique because it runs on bio-oil to efficiently generate heat. The plant has been operating commercially for more than a decade. Finland has conducted the majority of the research on bio-oil combustion in boilers. For example, Neste Oyj comprehensively tested a 2.5 MW boiler manufactured by Danstoker, equipped with a dual-fuel burner, which was run adequately at varying ratios of fuel oil to bio-oil [136]. Furthermore, in the absence of supplementary fuel, slight alterations to the pyrolysis oil were required to maintain CO_x and NO_x combustion emissions at reasonable scales (30 and 140 ppm, respectively), but particulate matter production was high (2.5–5 on the Bacharach scale) [137].

Likewise, Oilon Oy collaborated with VTT Energy to examine different types of bio-oils in an 8 MWth nominal furnace with a capacity of 4 MWth [138]. These findings were consistent with those reported by Neste Oyj. The following points are a brief description of the Oilon Oy and VTT Energy results:

- To promote combustion, changing the burner and boiler sections is necessary.
- The bio-oil combustion flame was longer than that produced by regular fuel oil combustion.
- Auxiliary fuel is required throughout the starting and operating stages, particularly when low-quality bio-oil is used.
- Obvious variances were noticed in the ignition of bio-oil and emissions.
- Overall, the emissions were lower than those from firing heavy fuel oil, with the exception of particulates. Emissions reduction depends heavily on proper handling of bio-oil (preheating to 50 °C and optimizing compressed air atomization) [139].

Combusting fossil fuels and bio-oil fuels could be attractive choices. Large-scale co-firing experiments were performed at a power station in Manitowoc, WI, USA, where coal was mixed with pyrolysis liquids synthesized by Red Arrow to generate electricity commercially. Handling problems (storage, pumping, filtration, and atomization) and optimization of the burner/boiler configuration to boost efficiency and minimize emissions can be resolved by making slight changes to the current equipment. However, large-scale industrial applications require a reliable supply of cost-effective, higher-quality bio-oil [142].

6.1.2. Combustion in Diesel Engines

Diesel engines can use diesel efficiently to generate a maximum power of 45%. Therefore, these engines are suitable for medium and slow combined-heat-and-power applications. Running diesel engines on bio-oils has raised critical concerns stemming from the basic attributes of such liquid fuels, such as troublesome ignition owing to their elevated water constituents and depressed calorific value, their corrosiveness arising from their acidity, and their tendency to coke owing to the presence of low thermally stable compounds [140]. Shihadeh investigated the combustion of pyrolysis oils derived from biomass on a Ricardian diesel engine, which injects fuel directly into its thumper with a capacity of 450 mL, operated at 19.8 and 2400 rpm [141]. In contrast to burning diesel while controlling its mixture with air, bio-oil combustion is predominantly kinetically regulated. However, considering this difference, bio-oils and diesel have similar thermal efficiencies, as verified by Ormrod [137].

6.1.3. Combustion in Turbines

At the beginning of the 1980s, Teledyne Technologies Incorporated was a pioneer in running gas turbines (J69-T-29 gas turbine combustor rig) using biomass-derived liquid fuels obtained by slow pyrolysis. They found that carbon monoxide emissions were higher, whereas CO_x and NO_x emissions were lower, than those emitted from burnt fuels derived from petroleum. Since 1995, Orenda Aerospace Corporation has effectively used bio-oil for combustion in a 2.5 MW electrical (MWe) Mashproekt gas turbine unit located in Ukraine [142]. Their study indicated that bio-oil combustion resulted in lower SO₂ and NO_x emissions over the entire operating cycle from idle to full power, but diesel produced fewer particulates than bio-oil. Finally, researchers at the University of Rostock in Germany burned bio-oil using a gas turbine of 75-kWe, where the engine was operated in the dual-fuel mode at 73% of the total power [142].

6.2. Application of Bio-Oils for Transportation Fuel

The best practice for utilizing bio-oil in transportation is to combine it with diesel. However, the pyrolysis oils derived from biomass are not miscible with petroleum-based fuels. Bio-oils derived from pyrolysis consist of a diverse combination of organic compounds such as acids, alcohols, aldehydes, ketones, ethers, furans, and phenols [144]. These components contribute to the unfavorable characteristics of crude bio-oil, including high corrosiveness, low heating value, and the inability to mix with petroleum-derived fuels [142], mainly owing to the high oxygen content (30–45 wt%), which renders it soluble in polar solvents and poses challenges for combining it with fossil fuels [145]. Moreover, the higher water content (15–30 wt%) of bio-oil than that of petroleum crude oil (just over 1% by weight), high acidity in the pH range of 2–4 [145], and other unfavorable characteristics (e.g., instability, high viscosity, inadequate combustion) make it unsuitable for industrial applications. The main cause of these disadvantages is the degradation of crude bio-oil by organic acids [144]. All these factors lead to the low stability of bio-oil, complicating its storage and transportation [145].

The addition of surfactants results in the formation of emulsions, thereby overcoming immiscibility obstacles. Compared with other technologies such as catalytic hydrogenation [146], catalytic esterification [147], and catalytic cracking [148], emulsification of bio-oil with petroleum diesel is a practical and highly efficient method for utilizing bio-oil [149]. By utilizing emulsifiers and co-emulsifiers, which can be either short- or long-chain alcohols, creating a stable and homogeneous system between bio-oil and diesel oil is possible [150,151]. Surfactants decrease the interfacial tension between bio-oil and diesel, facilitating the creation of a stable emulsion. This stabilization process inhibits phase separation and hence enhances the efficiency of the mixture as a fuel [152]. The use of surfactants in diesel–bio-oil emulsions can enhance the combustion efficiency in two ways: first, the heat of evaporation of water assists in lowering the maximum temperature during combustion, thereby reducing the emissions of NO_x ; and second, volatility and combustion are enhanced by generating micro-explosions during the combustion process [153]. Micro-explosions occur owing to the quick evaporation of water in bio-oil, resulting in improved fuel atomization and enhanced combustion efficiency. This approach can mitigate some of the adverse effects associated with the direct utilization of bio-oils [152].

An alternative route for making bio-oil suitable for transportation is through a deoxygenation process, which can be achieved via either hydrotreatment or catalytic vapor cracking. Hydrotreatment results in the removal of water (one of the oxygen forms), whereas the hydrogenation–hydrocracking of large molecules requires high temperatures, high hydrogen pressure, and a catalyst. Commonly used catalysts include alumina-supported cobalt molybdenum or nickel molybdenum sulfide, and their circumstances are analogous to those applied in petroleum processing [154]. Acidic zeolite catalysts are useful for catalytic cracking in the gaseous phase because dehydration and decarboxylation occur concurrently.

Chemicals derived from biomass typically have a higher oxygen-to-carbon ratio than the majority of petrochemical products, necessitating the removal of oxygen during primary valorization processes. Hydrogenolysis is a commonly used method for removing oxygen and reducing organic substrates by dissociating chemical bonds and adding hydrogen to molecular pieces [155]. Oxygen can be eliminated as H_2O from the oxygen-rich bio-oils via a catalytic hydrotreatment process, which requires catalysts possessing Brønsted acidity for dehydration or Lewis acid sites for binding the targeted molecule's oxygen ion pair and metal sites capable of activating hydrogen molecules. Bifunctional catalysts require Lewis acid sites to attract the oxygen ion pair of the target molecule, as well as Brønsted acidity and metal sites to activate the hydrogen molecules. Oxophilic metals, such as molybdenum (Mo), rhenium (Re), and tungsten (W), when mixed with nickel or noble metals such as palladium (Pd) or platinum (Pt), form highly catalytic and efficient systems for hydrogenation and dehydrogenation reactions, where nickel or noble metals promote hydrogenation, while oxophilic metals activate C–O bonds.

Oxophilic metals facilitate interactions between the catalyst and oxygenated biomass molecules by creating more robust interactions with oxygen atoms [156]. This strong interaction enhances oxygen removal during dehydrogenation and facilitates hydrogen activation during hydrogenation [157]. For example, during the deoxygenation of bio-oils, these metals play a crucial role in the effective removal of oxygen atoms, resulting in the production of high-quality hydrocarbon fuels. The interaction between metals with an affinity for oxygen (oxophilic metals) and noble metals or nickel (synergistic effects) is essential for enhancing catalyst stability and maximizing the efficiency and selectivity of biomass conversion into valuable products [158].

A prominent example is the upgrading of oil via the pyrolysis of oxygenated fuel over a bimetallic surface. The hydrodeoxygenation (HDO) of *m*-cresol in the presence of a

bimetallic Pt–Co surface supported on Al_2O_3 was affected by the synergistic effect of both metals, which enhanced the HDO mechanism in *m*-cresol. The Pt metal atom activated hydrogen, whereas the Co atom was oxophilic, activating the C–O bond. This combination resulted in 97.1% deoxygenation with a catalytic efficiency of 57% [97].

In another example, a combination of oxophilic metals, Rh– ReO_2 , was used as a bimetallic catalyst surface supported on SiO_2 for C–O activation. Glycerol was deoxygenated over Rh– ReO_2 with a catalytic efficiency of 10% and a deoxygenation rate of 22%. Rh is a hydrogen-activating metal, whereas ReO_2 interacts strongly with the C–O bond of glycerol [159].

Therefore, to improve the physicochemical properties of bio-oils, the designed catalysts must prefer the removal of oxygen by hydrogen treatment over hydrogenation reactions, which results in increased hydrogen consumption and a decrease in the octane number of the oil. Neutral supports appear to be a promising strategy for preventing coke formation under severe operational conditions [160]. Hydrogenolysis strategies for oxygen elimination require high quantities of hydrogen, which are usually supplied at high molecular pressures. Most hydrogen-producing technologies are energy intensive and nonrenewable. In situ hydrogen generation is an intriguing possibility; using hydrogen-producing molecules such as formic acid, which can be obtained from biomass, is a promising strategy [161].

For biomass conversion, bifunctional catalysis mostly involves both Lewis and Brønsted acid sites. Brønsted acids play a vital role, where protonation is necessary for the stabilization of charged intermediates in hydrolysis and dehydration processes. For example, in the conversion of cellulose, a complex carbohydrate polymer, into glucose or small, highly reactive compounds such as furans and levulinic acid, Brønsted acid sites protonate the hydroxyl groups of cellulose, in turn leading to the breakage of the glycosidic linkage. In addition, Brønsted acid sites are also used to convert fructose into relevant dehydrated products. In most of these cases, metal alloys and metal compounds can act as Lewis and Brønsted acid sites.

By contrast, Lewis acid sites stabilize anionic intermediates by accepting their electron pairs. In biomass conversion reactions, Lewis acids such as AlCl_3 promote acylation and aryl ketone formation. In such reactions, Lewis acids are utilized to stabilize the electron-deficient acyl cations. Thus, both Lewis and Brønsted acid sites are commonly used as bifunctional catalysts in hydrolysis and dehydration reactions [162].

In most cases, 5-hydroxymethylfurfural (HMF) is produced when both Lewis and Brønsted acid sites are present [163]. This coexistence is crucial for the Lewis-catalyzed conversion of glucose to fructose, followed by the formation of HMF over the Brønsted acid sites [164]. Weingarten et al. [165], along with other researchers [166], recently developed a novel mechanistic method for the production of HMF from cellulose/glucose using Brønsted acid catalysts. This pathway involves direct dehydration, which generates levoglucosan as an intermediate [164].

The synergy between Brønsted and Lewis acid sites in bifunctional catalysts is critical in optimizing the conversion process. Lewis acid sites, which function as electron-pair acceptors, play a crucial role in isomerization and deoxygenation reactions [162]. An example is the conversion of glucose to fructose through isomerization. This process is facilitated by the active sites of the catalyst, which induce polarization of the carbonyl group in the opened glucose ring. Consequently, an intramolecular hydride transfer between C_2 and C_1 takes place, forming fructose [162,167].

Beyond replacing diesel, bio-oil will become the basis for the future of new fuel-hydrogen transport systems. Researchers at The National Renewable Energy Laboratory (NREL) in Golden, Colorado, USA, thoroughly investigated the extraction of H_2 gas from

biomass via steam reforming or pyrolysis [168]. H₂ gas derived from steam reforming of an entire oil may be an attractive transport fuel in the future [137].

7. Potential Market for Bio-Oil

7.1. Market Situation

- The biofuel market is projected to reach \$225.9 billion by 2028, with an estimated 5.10% increase over a period of 7 years, starting in 2019. This CAGR is driven by environmental concerns about global warming and the need to decrease GHGs [169]. Global ethanol output is expected to reach ~166 billion liters by the end of 2024, with the USA and Brazil accounting for 80% of the production [170]. Global biodiesel production is expected to reach 50 billion liters by the end of 2024, with Indonesia, the EU, and Brazil leading the production [171].
- Owing to the renewability of biodiesel, the global demand for biofuels is expected to increase significantly between 2019 and 2025. According to the 2018 statistics of the World Bioenergy Association's Global Bioenergy, the leading sustainable solution for the transport sector is liquid biofuels, particularly biodiesel, because they are environmentally friendly. In 2016, 3.43 exajoules worth of biofuel were used in the transport sector.
- The world market is divided into ethanol and biodiesel based on fuel sources. In the global market, the ethanol segment is expected to dominate, with a growing demand for bioethanol as a car fuel because it can minimize GHG emissions [172].
- The global market is divided into first, second, and third generations according to the type of feedstock utilized. During the forecast period to 2025, the first generation would make a strong contribution owing to its lower saturated fat content, facilitating processing and thus reducing the total production cost. In addition, the feedstock required to produce vegetable oils is more easily obtainable than cellulosic and algal feedstocks.
- The growth of comparatively limited biofuel markets in other parts of the world depends on a combination of decided procedural backing and price patterns and has regional-based potential.
- The price and production costs of bioethanol and biodiesel depend on the feedstock. Cornstarch-based bioethanol in the USA costs approximately \$0.4–0.5/L [173]. Ethanol based on Brazilian sugarcane has better pricing power owing to lower feedstock and processing costs. The approximate cost is \$0.20/L [174]. The price of European sugar beet ethanol is approximately \$0.82/L. The ethanol production cost from second-generation LCB remains relatively high, at \$1/L [175].
- The production cost of biodiesel depends on feedstocks such as soybean, palm oil, and canola oil. The global average cost for biodiesel is approximately \$0.35–0.65/L. Low-cost feedstocks such as waste cooking oil or animal fats can reduce costs further, but the supply is limited. Third-generation biodiesel is the most expensive, with a cost as high as \$2.5/L [176].
- Biofuel plants require high capital investment. For instance, a 190-million-per-year corn-based ethanol refinery would cost up to \$75 million in CAPEX annually. Lignocellulosic ethanol facilities are far more expensive because more sophisticated processes are required. With the progress in technologies and scale-up of plants, these capital costs can be significantly reduced, but the cost will continue to be high in comparison with first-generation plants. Biodiesel plants and refineries are simpler and smaller, making them more cost-effective. Overall, investments of around \$140 million in ethanol plants and \$120 million in biodiesel plants are required. Capital costs significantly vary across countries and regions [177].

7.2. Price

The assessment of the economic viability of biofuels in comparison with fossil fuels relies heavily on the analysis of production costs. The feedstock cost, which is determined by factors such as agricultural productivity, geographical supply, and market requirements, plays a crucial role in the entire cost structure. The difficulty of converting biomass into biofuels directly affects processing costs, with advanced biofuels necessitating more advanced technologies. Typically, biofuels are expensive when judged on an energy-equivalent basis [178,179]. However, this comparison is changing owing to developments in technology, carbon pricing mechanisms, and government subsidies and incentives [180]. The economic viability of biofuels is also affected by external factors such as crude oil prices. When oil prices are high, biofuels become more appealing; however, their competitiveness is compromised when oil prices are low. The ability to scale up biofuel production depends on the availability of sustainable feedstocks, which may pose constraints in certain areas. Ultimately, despite the current higher production costs of biofuels than fossil fuels, continuous technological advancements, favorable regulations, and environmental factors are progressively improving their economic viability [178,181].

Given the expansion of the crude oil market and revival of biofuel feedstock prices, the prices for ethanol and biodiesel are anticipated to rebound in titular terms by 2025 as illustrated in (Figure 4) [182]. The nominal prices of biodiesel are expected to rise at a lower rate ($\sim 0.8\%$ per year) than ethanol prices ($\sim 2.4\%$ per year) owing to market developments involving vegetable oil, as indicated by (Figure 4). After 2025, ethanol prices are projected to return to a downward trend or remain stable, whereas biodiesel prices are projected to decrease or remain stable until 2031. The costs of producing bioethanol are declining; thus, market circumstances are currently favoring bioethanol over biodiesel [182].

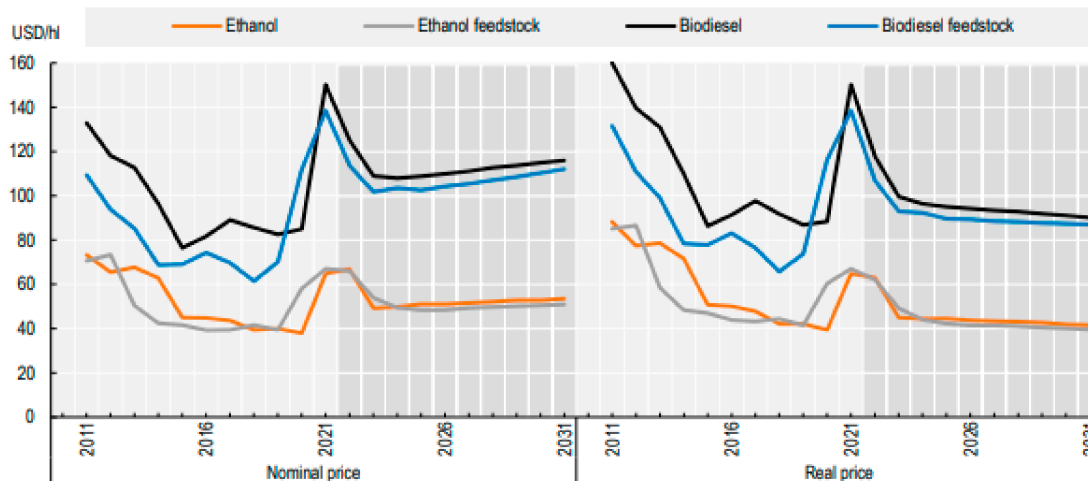


Figure 4. Price development of feedstock and biofuel from 2011 to 2031 [156].

National support policies have boosted biofuel market growth. The European Union and the United States, the two main manufacturing areas, increasingly support advanced biofuels that are not derived from conventional agriculture as feedstock. The International Energy Agency (IEA) World Energy Outlook foresees lower fuel demand in both regions, limiting ethanol growth. The projected developments in biofuel demand in the major regions are shown in Figure 5 [182]. Owing to the expected decrease in diesel usage, EU biodiesel utilization will likely dip below current levels. By contrast, vegetable oil-derived biodiesel is considered a biofuel under renewable fuel standard (RFS) regulations. The development of biodiesel mandates has been increasing in recent years, which should support the growth in US usage. The global transport sector is a significant driver of biofuel

production and utilization. The IEA World Energy Outlook [4] predicts that world gasoline demand will remain at approximately 1120 billion liters (bln L), whereas diesel demand will drop by 8% to 703 bln L. Despite this prediction, fuel demand is expected to continue to increase in many nations [182].

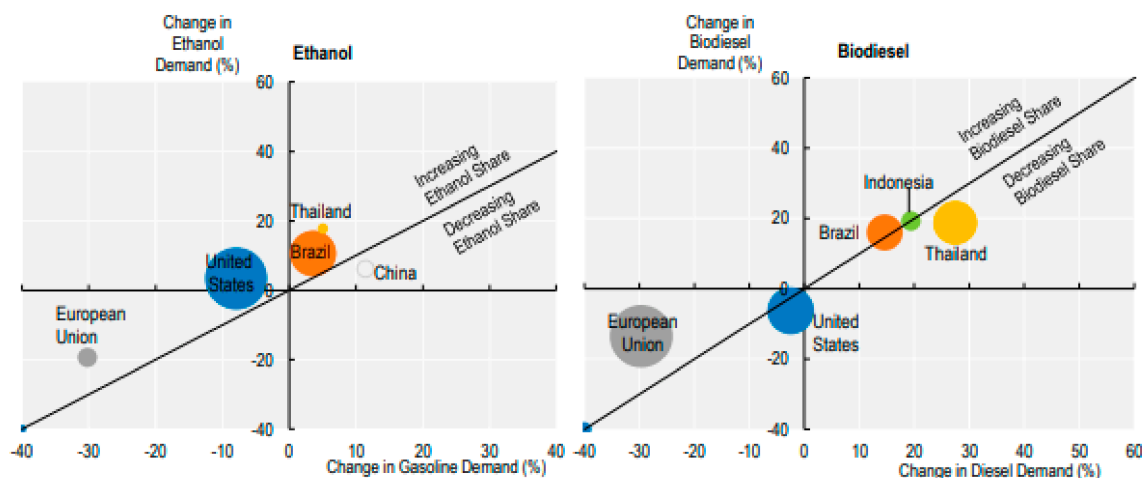


Figure 5. Projected developments in biofuel demand in major regions from 2022 to 2032 [182].

7.3. Production

Technological advancements have resulted in a global increase in biofuel production. Hydrothermal liquefaction, pyrolysis, and gasification are among the most common methods of biomass conversion, enhancing efficiency and making production more economically viable. These technologies facilitate the utilization of a broader range of raw materials, including agricultural residues and non-food crops, thereby reducing competition for food production [183,184]. Integrated biorefineries are being constructed to efficiently generate numerous products from a single biomass source, thereby reducing waste and improving economic viability [185]. However, challenges remain to be resolved, including the high cost and limited supply of feedstock as well as the ambiguity of policies and regulations. These factors have the potential to impede investment in biofuels technologies, resulting in market instability [181,186].

Biomass-derived fuels (biofuels) include bioethanol and biodiesel. Table 4 outlines the ranking of biofuel production by country and main feedstock. Currently, corn accounts for 60% of ethanol production, sugarcane for 25%, wheat for 4%, molasses for 7%, and other grains such as cassava and sugar beets for the remaining 4% [182]. Approximately 30% of global biodiesel is generated from soybean oil, 25% from rapeseed oil, 18% from palm oil, 10% from recycled vegetable oils, 6% from fats, and 11% from other vegetable oils [182].

Sugarcane and coarse cereals are the most prevalent ethanol feedstocks. In India, the use of molasses is foreseen to rise for the manufacture of ethanol. Vegetable oil remains the preferred feedstock for biodiesel production as demonstrated in Figure 6. In the US and EU, biodiesel production based on non-agricultural feedstock, specifically residual oil and tallow, is expected to rise. By 2025, ethanol derived from LCB is expected to generate less than 1% of the global ethanol production. The manufacture of biofuels is anticipated to utilize 10.4% of world coarse cereal production and 12.0% of global vegetable oil production by 2025. Approximately 22% of the world's sugarcane production is expected to be utilized in ethanol manufacturing by 2025 [182].

Table 4. Biofuel manufacture ranking and key feedstocks [187].

Country/Region	Manufacture Ranking (Base Period)		Main Feedstocks	
	Ethanol	Biodiesel	Ethanol	Biodiesel
United States	1 (46.7%)	2 (18.4%)	Maize	Soybean oil/used cooking oils
European Union	4 (4.9%)	1 (30.7%)	Maize/wheat/sugar beet	Rapeseed oil/palm oil/used cooking oils
Brazil	2 (26.3%)	4 (13.1%)	Sugar cane/maize	Soybean oil
China	3 (8.4%)	8 (2.8%)	Maize/cassava	Used cooking oils
India	5 (2.9%)	14 (0.4%)	Molasses/sugarcane/maize/wheat/rice	Used cooking oils
Canada	6 (1.6%)	13 (0.8%)	Maize/wheat	Canola oils/used cooking oils
Indonesia	20 (0.1%)	3 (17.5%)	Molasses	Palm oil
Argentina	8 (0.9%)	5 (3.6%)	Maize/sugar cane/molasses	Soyabean oil
Thailand	7 (1.4%)	7 (3%)	Molasses/cassava/sugar cane	Palm oil
Colombia	14 (0.4%)	11 (1.3%)	Sugar cane	Palm oil
Paraguay	11 (0.5%)	18 (0.02%)	Maize/sugar cane	Soybean oils

(Percentage values represent the country's portion of overall production during the reference period through 2028.)

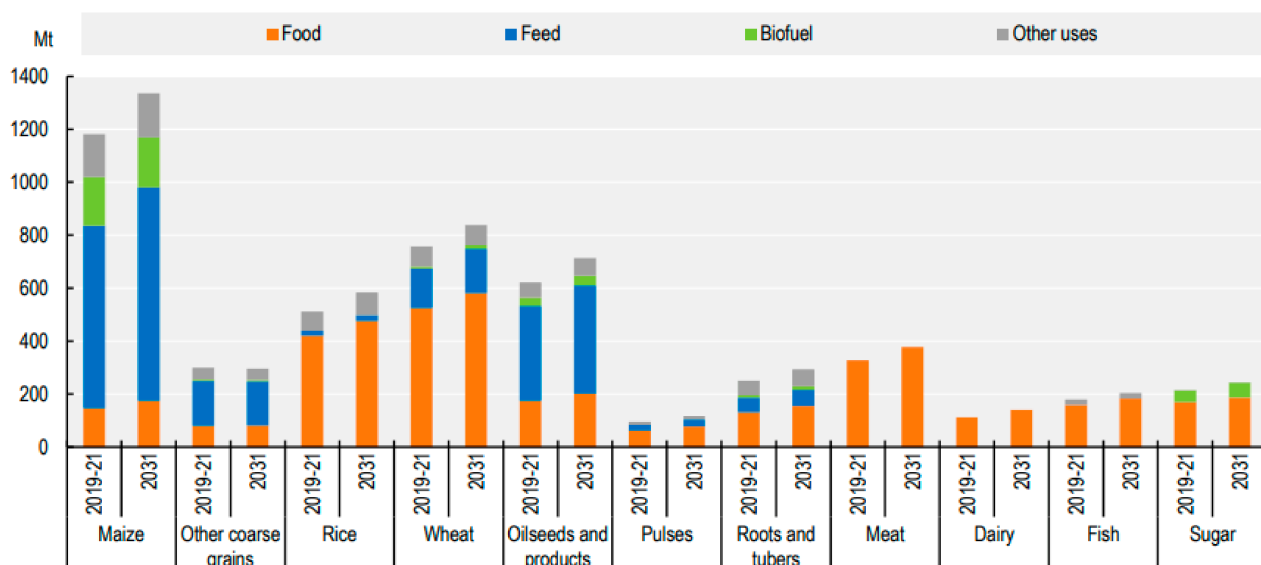


Figure 6. Biofuel production from various commodities and feedstocks in 2019–2021 and 2031 [156]. (Sugar crops include sugar cane and sugar beets in the European Union for the production of bioethanol.)

Global ethanol production is predicted to increase gradually from 116 to 128.4 bln L by 2025 [182]. The share of biofuels in total agricultural feedstock and commodities is shown in Figure 7 [182]. This increase is mainly anticipated in Brazil, primarily to meet domestic demand. Thailand is the second largest producer of biofuels. Ethanol production in the US is predicted to rise owing to the low prices of crude oil and high gasoline usage, and then fall owing to lower demand for transportation fuels. Despite this forecast, the US is anticipated to maintain its first rank in ethanol production and exports, followed by Brazil. Global biodiesel production is expected to be led by policies in the US, Brazil, Argentina, and Indonesia, and to a lesser degree by the European Union's Renewable Energy Directive (RED) goal. Biodiesel production is predicted to increase from 31 to 41.4 bln L by 2025.

Accordingly, the changes in ethanol and biodiesel consumption in the key regions are shown in Figure 8 for 2009–2031.

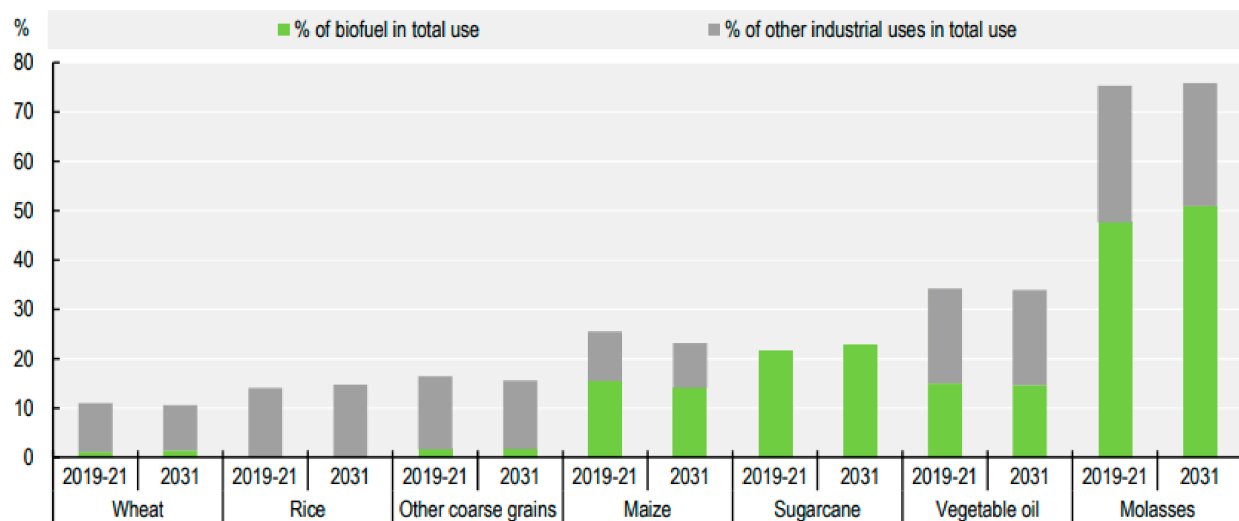


Figure 7. Share of biofuels in total agricultural feedstock and commodities [156].

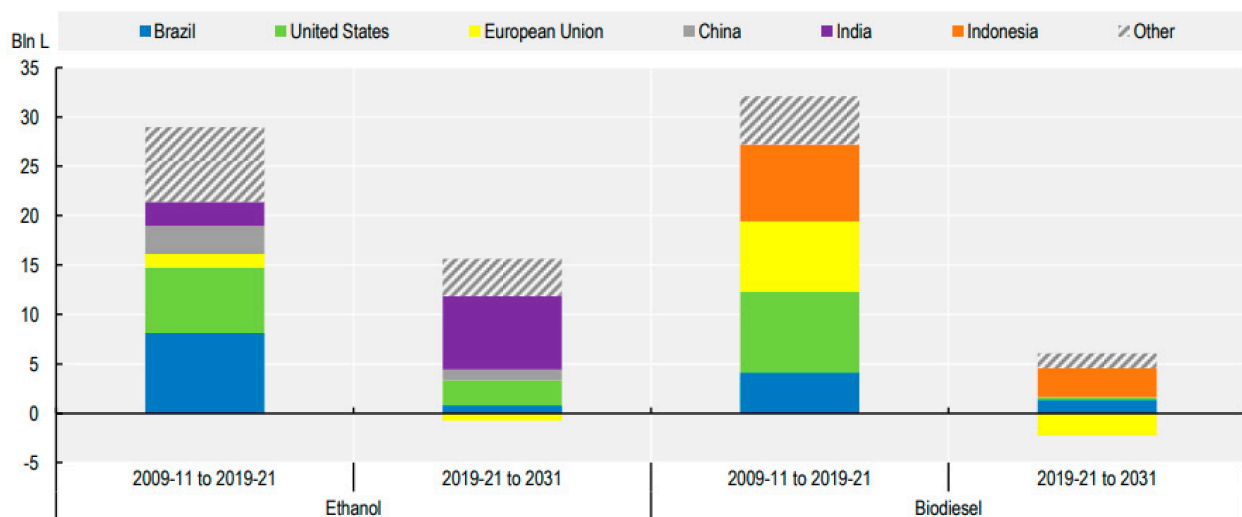


Figure 8. Changes in ethanol and biodiesel consumption in the key region from 2009 to 2031 [156].

The outlook predicts slower worldwide biofuel output growth than in earlier decades. The leading cause is that US and EU biofuel policies are decreasing. Given the expected growth of the transportation fleet and domestic policies favoring customer demand and higher blends, biofuels are expected to rise in major developing countries. Global production of biodiesel is expected to hit almost 44 billion L by 2028, while global ethanol production is expected to rise from 122 to 143 billion L by 2028, owing to the US mandate increase. Despite the growing awareness of biofuel sustainability in many nations, traditional feedstocks (biofuels derived from food and feed crops) dominate global biofuel production, as illustrated in Figure 9 [187]. The ethanol feedstock retained coarse grains, notably maize and sugarcane. By 2028, ethanol production will consume 14% maize and 24% sugarcane. Biodiesel production is expected to continue using vegetable oil as the primary feedstock, while waste oil and tallow biodiesel will remain essential in the EU, Canada, and the US.

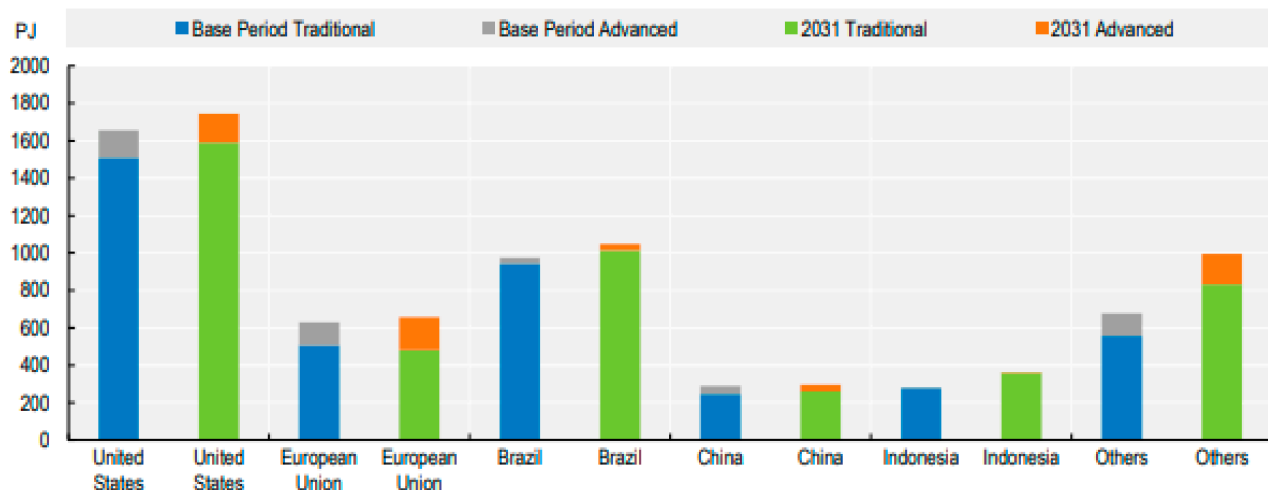


Figure 9. Production of biofuels globally from conventional and innovative feedstocks, 2022–2031 [155]. (Conventional feedstocks include biofuels derived from food and fodder crops. The unit used was petajoules (1015 joules).)

Brazil is the only nation in which the proportion of energy entering the transportation sector through biofuels exceeds 10%. Nevertheless, a common objective of biofuels policies, particularly in developing nations, is to minimize fossil fuel reliance, a goal that has not yet been attained in most nations. Indonesia aims to meet the B30 goal of decreasing the country's reliance on fossil fuels by increasing the blending rate from the current 8% in the base period to a target of 13% by 2028 (5.8 bln L). This outlook predicts a rise in the consumption of ethanol and biodiesel (Figures 10 and 11) [182]. The primary objectives in India are to increase the ethanol and biodiesel blend rates to 20% and 5% from their present levels of 1.4% and 0.1%, respectively. Argentina has a blending mandate for 12% ethanol and 10% biodiesel. Thailand seeks to reduce its carbon dioxide emissions and reliance on fossil fuels. Owing to feedstock availability issues, its ambitious aim is to produce 4.1 bln L of biodiesel and reduce ethanol to 2.6 bln L. In the US, biodiesel production is anticipated to grow to 8.7 bln L. The annual increase in ethanol production is expected to reach 0.1%. This view does not predict a significant export of biofuels from the US. Although the US remains the leading ethanol manufacturer worldwide, its global production share is expected to decline from 50% to 43%.

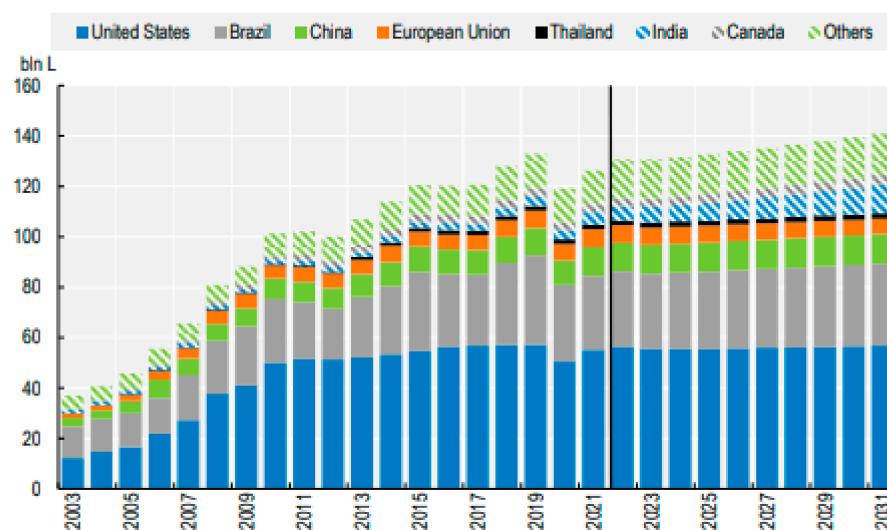


Figure 10. Development of world ethanol consumption, base period to 2031 [182]. (Blue shading indicates reduction.)

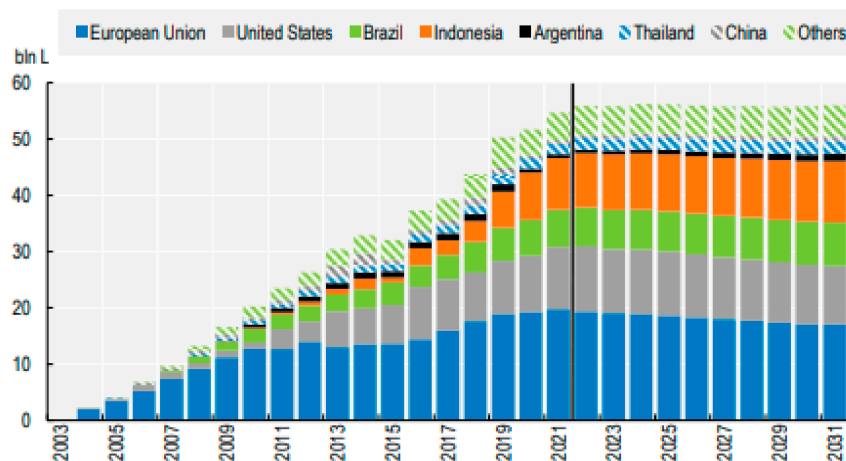


Figure 11. Development of world biodiesel consumption, base period to 2031 [182].

The productivity and sustainability of biomass-based biofuel production are connected to maintaining natural resources, mitigating GHG emissions, and restricting pollutant discharge. Such a goal can be achieved by maintaining the reserves of water and soil, preserving the amounts of nutrients and organic matter in the soil, recycling the nutrients, and limiting the release of all types of contaminants to the atmosphere, surface and ground water, and soil. These practices ensure the flourishing of the agricultural sector, which is the sole source of biomass. However, hard work and implementation of adequate legislation are essential for sustaining biomass and biofuel production [188]. Moreover, countries should align themselves by applying global policies and clear practices to increase biofuel production and investment.

7.4. Barriers to Large-Scale Deployment

However, biofuels face various economic and policy challenges. Some of these challenges are explained below.

- The capital costs of biofuel refineries are high. A high CAPEX indicates that investors take higher financial risks with longer payback time. Cellulosic plants have even higher costs, which can be reduced by targeted policies and subsidies. Ethanol and biodiesel production require specialized equipment, distribution, and process infrastructure. Dedicated piping and tankers are required for the transportation and distribution of biofuels. The expansion of biofuels requires significant investments in fuel logistics and vehicles.
- Biofuel markets depend largely on various policies, including tax credits, blending mandates, and carbon regulations, and these differ substantially from region to region. In the United States, the Biodiesel Tax Credit (\$0.26/L) supports producer economics, alongside Renewable Fuel Standard (RFS) blending obligations. The European Union regulates biofuels primarily through its Renewable Energy Directive (RED III, in force since November 2023), which raises the EU-wide renewable energy target to 42.5% by 2030 and sets a 29% renewable-energy target specifically for the transport sector, up from 14% under RED II. RED III also caps food and feed crop-based biofuels at 7% of transport energy and requires existing and new production facilities to achieve GHG savings of at least 70% and 80%, respectively, relative to fossil fuels [189]. Individual EU member states implement these targets through blending mandates and excise duty exemptions. For example, Slovakia mandates a minimum of 6.9% biodiesel content in diesel fuel, while Spain targets 28% renewable energy in transport by 2030 [190]. Outside the US and EU, Indonesia is the largest palm oil-based biodiesel producer and operates a mandatory blending program (B40, 40% palm-oil-derived

FAME blended with diesel), supported by government subsidies exceeding USD 3 billion in 2025 and funded through palm oil export levies. The government has plans to raise the mandate to B50 [191]. These policies (direct tax credits in the US, binding renewable-energy and GHG-reduction targets in the EU, and blend-mandate-plus-subsidy models in Indonesia) show that biofuel market growth is highly sensitive to region-specific regulations, and any change in policies in any of these major markets could significantly disrupt global biofuel investment and trade flows.

- Biofuels show promising prospects to reduce GHG emissions, but their actual environmental benefits are heavily dependent on the choice of feedstock and land-use policies. Life-cycle assessments of US soybean biodiesel report GHG emission reductions of approximately 76% relative to petroleum diesel when land-use change is excluded, falling to 66–72% when induced land-use change (ILUC) is considered, with reported reductions across various oilseed and waste-fat feedstocks ranging from 40% to 86% [192,193]. On the other hand, palm oil-based biodiesel shows a more complex picture. While cultivation on already degraded land with methane capture can achieve strong GHG reductions, scenarios involving deforestation or peatland conversion can result in net GHG emissions considerably higher than those of fossil diesel [194]. This feedstock dependence means that blanket claims of biodiesel environmental benefit should be qualified by feedstock origin and land-use history. Beyond GHG accounting, large-scale bioenergy crop cultivation raises broader sustainability concerns through the energy-water-food nexus. Irrigation-intensive feedstocks can strain regional water supplies, while diverting arable land toward energy crops competes directly with food security and can elevate food prices, particularly in food-scarce regions [195]. Economically, these environmental trade-offs are increasingly reflected in policies such as the EU RED III GHG-savings thresholds and feedstock eligibility criteria, which explicitly restrict food-based feedstocks and reward advanced, nonfood-based feedstocks. This is how economic incentives are being realigned to account for these environmental trade-offs [189].

8. Conclusions

Sustainable development of biomass from lignin, cellulose, or hemicellulose can potentially secure sustainable energy and bridge the gap in continuous energy demand. The sustainable development of biofuels from LCB offers a promising framework for meeting global energy demands while addressing environmental issues. Lignocellulose-based fuels, such as ethanol, bio-oil, biogas, syngas, and biodiesel, are produced through advanced thermochemical and physicochemical processes, such as pyrolysis, gasification, liquefaction, esterification, and transesterification. The efficiencies of these processes are often enhanced using bifunctional and bimetallic catalysts. These processes enable the production of both energy and high-value chemicals, thereby improving the economic viability of biofuel production.

Current and future projections indicate increased production of biofuels, with a further increase in supply and demand in the coming years. Most countries aim to decrease their reliance on fossil fuels by seeking alternatives such as ethanol and biodiesel. Increasing research and technological advancements indicate a bright future for biofuels. Despite these positive developments, biofuel production still faces certain challenges and limitations. The scalability of biofuels is hindered by issues such as limited food and water resources, land-use concerns, and high capital and operational costs for large-scale plants. Moreover, uncertainties regarding the policies and technological limitations of third-generation biofuels remain key barriers.

9. Comparative Analysis and Future Prospects

First-generation biofuels are produced from agricultural feedstocks and edible crops. These biofuels offer a higher yield and efficiency but have certain limitations, including food security issues and long-term sustainability concerns. Second-generation biofuels are produced from non-food-based LCB while addressing the issues and limitations of first-generation biofuels; however, they require high-cost pretreatment processes and complex conversion technologies. Third-generation (e.g., algae) and fourth-generation (e.g., carbon capture-integrated systems) biofuels have shown promising results, with higher productivity, efficiency, and near-zero carbon emissions. Both generations of biofuels are in their early developmental phases and require further research.

Research on catalyst design, integrated biorefineries, and energy-efficient conversion processes, such as MW-assisted and hydrothermal processes, can significantly reduce costs and improve yields. Policies favoring carbon pricing, tax incentives, and the implementation of the United Nations' Sustainable Development Goals will be an important driving force for the commercial-scale deployment of these biofuel technologies. The transition to sustainable green biofuels depends on continuous innovations to enhance process efficiency, overcome food security issues, and align these technologies with circular economic principles. Integrated research, new investments, and efficient policy frameworks can enable lignocellulose-based biofuels to play an important role in decarbonizing global energy systems in the coming decades.

Another point to be considered is political crises and wars as a driving force for increasing demand and dependence on biofuels due to the short supply of fossil fuels (oil and gas) in the market around the globe. For instance, the current situation in the Gulf region hinders the export of oil and gas through the Strait of Hormuz, leading to an increase in their prices and forcing dependence on biofuels to accommodate energy needs.

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Abbreviations

The following abbreviations are used in this manuscript:

LCB	Lignocellulosic biomass
GHG	Greenhouse Gas
SCFs	Supercritical Fluids
ILs	Ionic Liquids
TAN	Total Acid Number
FAME	Fatty Acid Methyl Ester
WCO	Waste Cooking Oil
RSM	Response Surface Methodology
WNS	Walnut Shell Powder

NREL	National Renewable Energy Laboratory
IEA	International Energy Agency
RFS	Renewable Fuel Standard
RED	Renewable Energy Directive

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