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Review

Drivers and Barriers in the Production and Utilization of Second-Generation Bioethanol in India

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Abstract: Second-generation biorefinery refers to the production of different types of biofuels, biomaterials, and biochemicals by using agri-based and other lignocellulosic biomasses as substrates, which do not compete with arable lands, water for irrigation, and food supply. From the perspective of transportation fuels, second-generation bioethanol plays a crucial role in minimizing the dependency on fossil-based fuels, especially gasoline. Significant efforts have been invested in the research and development of second-generation bioethanol for commercialization in both developing and developed countries. However, in different developing countries like India, commercialization of second-generation bioethanol has been obstructed despite the abundance and variety of agricultural feedstocks. This commercial obstruction was majorly attributed to the recalcitrance of the feedstock, by-product management, and marginal subsidies compared to other nations. This article reviews the major roadblocks to the viability and commercialization of second-generation biofuels, especially bioethanol in India and a few other leading developed and developing nations. This article also reviews the biomass availability, technological advancements, investments, policies, and scale-up potential for biorefineries. A thorough discussion is made on the prospects and barriers to research, development, and demonstration as well as strengths, weaknesses, opportunities, and threats for the commercialization of second-generation bioethanol.

Keywords: bioethanol; biochemicals; biofuels; commercialization; lignocellulosic biomass; policies; scale-up; second-generation biorefinery

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1. Introduction

The global energy demand is seeing a significant escalation because of population growth and the industrial and economic progress seen in emerging nations like China and India. The current situation is characterized by growing concerns over greenhouse gas emissions, uncertainties relating to energy security, increasing fossil fuel prices, and geopolitical situations [1]. Renewable energy sources such as solar, hydro, tidal, wind, geothermal, and biomass-based energy have garnered heightened interest as potential substitutes for nonrenewable sources [2]. Nevertheless, the need for platform chemicals produced in petroleum refineries may only be substituted by renewable bioresources, namely refineries based on lignocellulosic biomass.

Lignocellulosic biorefineries are seeing a progressive global expansion whereby biomass is being used as a sustainable energy source [3]. The term lignocellulosic biorefinery pertains to a kind of biorefinery known as a second-generation biorefinery, whereby lignocellulosic biomass is used as the primary feedstock material. Lignocellulose is a plentiful and carbon-neutral bioenergy resource in comparison to conventional fossil fuels. Massive potential exists for lignocellulosic biomass to serve as a partial substitute for fossil fuels, petrochemicals, and synthetic plastics in the energy and consumer product market and meet sustainability [4]. The implementation of biorefineries offers a viable solution for the conversion of biomass into a diverse range of products, including high-value commodities and biofuels [5].

Figure 1 illustrates the many pathways involved in the production of several by-products in a second-generation biorefinery using lignocellulosic biomass. The methodological approach for the valorization of lignocellulosic biomasses to second-generation liquid biofuels, especially bioethanol, is constituted of three major steps: (i) partial disintegration of the recalcitrant moieties of the feedstock through pretreatment techniques, (ii) production of monomeric sugar hydrolysate from the fragmentation of biopolymeric matrix, and (iii) fermentation of monomeric sugars into alcohols [6]. Besides the fermentative or biochemical conversion, thermocatalytic routes can also be employed in the making of bioethanol to produce different platform chemicals like furfurals, phenolics, and levulinic acid.

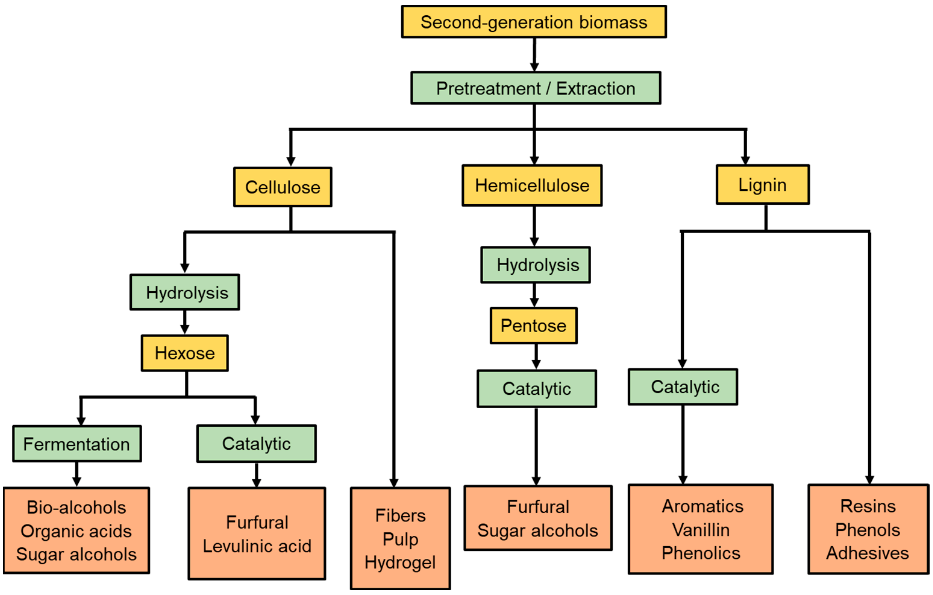

Figure 1. Bioproducts obtained from second-generation biorefinery of lignocellulosic biomass.

The predominant practice for managing lignocellulosic biomass, especially in developing countries, is direct combustion, which leads to the inefficient use of resources and air pollution [7]. Hence, the development of alternative technologies is essential to enhance the responsible usage, management, and valorization of lignocellulosic biomass [8]. The use of lignocellulose as a potential substitute is supported by its abundant and diverse sources of raw materials, as well as the advantageous market prospects of its conversion products. The primary components of biomass, including cellulose, hemicellulose, and lignin, play a crucial role in the biorefinery system and significantly contribute to the overall expansion of the global bioeconomy [9,10]. The generation of sugar monomers can be achieved using cellulose and hemicellulose, which are the polysaccharide constituents found in lignocellulosic biomass. The efficiency and cost-effectiveness of the bioconversion process are contingent upon the extent to which polysaccharides are effectively converted into monomeric sugars and subsequent fermentation to biofuels and biochemicals [11].

The upscaling of biochemicals and biofuel production from lignocellulosic biomass continues to pose significant problems, necessitating the resolution of many fundamental operational obstacles. The primary obstacle to the efficient use of biomass is the intricate recalcitrance and structure of lignocellulosic biomass [12,13]. The limited production of fermentable sugars could be attributed to the presence of lignin polymer and the common component of lignocellulosic feedstocks, which act as barriers to the nonspecific binding of hydrolytic enzymes [14–16]. To address these concerns, it is necessary to include lignin removal as an additional pretreatment step. This step is essential for eliminating the refractory nature of lignocellulosic biomass and facilitating its further processing [17]. Numerous pretreatment methods have been proposed over recent years to generate fermentable sugars effectively [13,18,19]. However, pretreatment is a costly and energy-intensive process that has a significant influence on the economic competitiveness of lignocellulosic biorefineries. The economic feasibility of the biomass market and supply chain, the level of technological advancement of the utilized technologies, and the transition from laboratory-scale to pilot-scale processes are additional significant obstacles that hinder the commercialization of lignocellulosic biorefineries [9,20].

The process of expanding biorefinery operations from a laboratory setting to a commercial scale is intricate and requires significant financial investment. Similarly, the optimization of energy efficiency and the effective management of waste by-products are imperative technical endeavors. Economic hurdles encompass several factors, such as substantial upfront investment requirements, the challenge of maintaining economic sustainability in the face of volatile oil prices, and the scarcity of available financing alternatives [21]. The prioritization of environmental sustainability and the active involvement of local communities is of utmost importance [22]. Developing countries have notable hurdles and roadblocks concerning the diversification of biomass sources, the scaling up of biorefinery technologies, and the commercialization of biofuels [23]. The restricted spectrum of biomass sources is mostly attributed to the geographical diversity of feedstocks with a heavy reliance on agricultural residues and a lack of awareness of sustainable waste management practices [24]. Addressing these obstacles and filling the gaps in knowledge is imperative to fully harness the promise of biofuels in the area and advance a sustainable, low-carbon energy trajectory.

The focus of this article is to shed light on the regulatory measures, policies, research advancements, and socioeconomic aspects of biomass utilization to produce biofuels in India with reference to a few other leading economies. While numerous reports are available in the literature on various aspects of biorefineries, the emphasis of this article is specifically on second-generation biorefineries that require lignocellulosic feedstocks without competing with food or fodder production, arable land, and water required for irrigation. Moreover, this review elucidates the primary obstacles encountered in biomass supply chains and biofuel commercialization, which are crucial factors in shifting the paradigm from fossil fuels to renewable energy.

2. Different Generations of Biorefinery

The notion of biorefinery has garnered considerable interest as a viable approach to achieving sustainable resource usage and the generation of biobased commodities [25]. A biorefinery refers to a comprehensive and interconnected system that transforms biomass into a diverse range of valuable biobased commodities, including biofuels, biochemicals, and biomaterials [26]. The initial wave of biorefineries prioritized the use of food crops for biofuel production. However, a more sophisticated and environmentally conscious approach has been adopted by second-generation biorefineries. These newer facilities aim to minimize the conflict between food and fuel production by utilizing lignocellulosic biomass. This shift in focus not only addresses environmental concerns but also enhances overall efficiency.

Concern about greenhouse gas emissions and the demand for energy resources results in shifting global attention towards biofuel production. As mentioned earlier, there are different generations of biofuels categorized based on their raw materials and production methods, such as the first, second, and third generations of biofuels [27]. The first-generation biomasses are mostly food crops such as corn, wheat, barley, sugar beet, sugarcane, paddy, and potato that are cultivated as energy crops to produce biofuels such as bioethanol [28]. These biofuels are produced through the fermentation of starch, a simple sugar present in these food crops and grains. However, the industrial production of first-generation bioethanol can be unethical and impact the socioeconomic aspects of biorefinery since it creates a food-versus-fuel scenario and competes with food supply and arable farms as well as nutrients and resource input [29].

Second-generation biorefineries predominantly utilize lignocellulosic feedstocks, including agricultural residues, forest residues, dedicated energy crops, and municipal solid waste [30]. These feedstocks are abundant in nature and inexpensive. The change in the selection of feedstock resolves problems of food security and competition for land usage. The feedstocks commonly encompass lignocellulosic materials, which necessitate more intricate processing methods owing to their inherent resistance. Lignocellulosic biomass comprises cellulose, hemicellulose, and lignin. It requires intensive methodologies for the effective separation and conversion of these components. The generation of biofuels needs development at a competitive cost due to more technical obstacles that must be overcome [31]. Second-generation biorefinery has become more attractive than traditional petroleum-based refineries due to liquid fuel substitutes, biobased materials, and bioproducts.

Third-generation biofuels are generally extracted from marine resource supply chains such as microalgae and water hyacinth [32]. Algal biomass is ideal for the generation of biofuels because of its photosynthetic properties to fix CO_2 biologically, produce lipid-based fuels and products, and utilize wastewater as a growth substrate [33,34]. Based on the size and morphology, algae are classified as macroalgae (up to 60 m) and microalgae (5–100 μm) [35,36]. However, microalgae have some important features, such as the ability to grow in all environments, produce high lipid (oil) content, and require relatively fewer nutrients to grow. The unique advantage of microalgae is the capability for both hydrogen production and oxygenic photosynthesis while capturing CO_2. Zhou et al. [37] reported that around 1.8 kg of CO_2 was consumed by 1 kg of algal biomass during production. However, the oil produced from algae has a high unsaturation level, which makes it more volatile and susceptible to denaturation at high temperatures [38]. Because algae have a short growth cycle, more biomass precursors can be harvested at a rate faster than that of other energy crops (e.g., switchgrass and hybrid poplar) and other first- and second-generation feedstocks. Additionally, since algae may thrive in industrial effluent and wastewater, there is a limited requirement for fresh, clean water [39].

One of the primary obstacles encountered in second-generation biorefineries is the enzymatic hydrolysis of the intricate lignocellulosic matrix to extract its constituent components. Numerous investigations have been made to achieve this goal by applying biological, chemical, thermal, or hydrothermal processes [40–42]. Since all conversion techniques face some difficulties, chemical processes are recognized as the most suitable, considering the faster and more flexible conversion of biomass to biofuels and biochemicals [43]. Various pretreatment methods, such as steam explosion, acid hydrolysis, and enzymatic treatments, are utilized to weaken the structure of biomass and enhance the extraction of cellulose, hemicellulose, and lignin components [44]. The optimization of pretreatment processes is crucial to achieving high product yields and minimizing the formation of undesired by-products that can impact the downstream processing and fermentation process [45].

Second-generation biorefineries utilize several conversion methods to convert the recovered biomass fractions into products that are derived from biological sources. Enzymatic hydrolysis is a widely employed process in which cellulose and hemicellulose are enzymatically degraded into fermentable sugars [46]. These sugars can then be utilized for the formation of bioethanol and other biochemicals. The biological conversion of biomass entails the following key steps: (i) selection and processing of biomass, (ii) pretreatment of biomass, (iii) biomass saccharification, (iv) fermentation of pentose and hexose, and (v) downstream operations [20,47,48]. On the other hand, thermochemical conversion techniques, namely, liquefaction, pyrolysis, and gasification can transform lignocellulosic materials into biofuels in the form of solid (biochar), liquid (bio-oil and biocrude oil), and gas (syngas and hydrogen) [49].

One distinguishing characteristic of second-generation biorefineries is their adaptation of an integrated strategy toward achieving maximum product diversity. These biorefineries strive to optimize the extraction of high-value from low-cost feedstocks by utilizing a combination of chemical, biological, and thermochemical processes [50,51]. For example, lignin is commonly seen as a secondary product within the pulping industry. However, it has the potential to be transformed into valuable biochemicals and biomaterials such as biobased polymers and adhesives [52,53]. However, from a commercial point of view, the integration of different biological and thermochemical conversion processes may deliver a more sustainable process for the industrial production and utilization of biomass-derived products in a circular approach. For instance, Giuliano et al. [54] proposed an integrated process for the valorization of biomass by producing multiple products like levulinic acid, succinic acid, and bioethanol by using both the thermocatalytic and biochemical conversion routes. Multiple product-based biorefineries could be more feasible than single-product biorefineries, which has become one of the main future visions of second-generation biorefineries.

Second-generation biorefineries play a significant role in promoting sustainability through the mitigation of greenhouse gas emissions, the reduction of dependence on fossil fuels, and the efficient utilization of waste materials [55]. These benefits also serve as the fundamental aspects of a circular economy since they involve the use of waste streams and the production of biobased commodities with a significantly low impact on the environment. Nevertheless, it is imperative to tackle the obstacles associated with the availability of feedstock, energy consumption throughout the process, and economic feasibility to guarantee the enduring sustainability of these biorefineries. These lignocellulosic-based, second-generation biorefineries aim to establish a sustainable and diverse biobased economy by employing lignocellulosic feedstocks, modern conversion technologies, and an integrated circular economy strategy.

3. Second-Generation Biorefinery in India and Other Leading Economies

Asian countries like India and China are the major contributors to the second-generation feedstock. India is a prominent global producer of food grains, generating a substantial amount of agricultural waste each year estimated at 1043 million metric tons [56]. The major portion of the agricultural residues solely from the Asian countries rely on the intensive agricultural practices throughout the different regions. Besides India and China, Brazil is the leading producer of sugarcane in the world, which generates around 780 million metric tons of bagasse and pith [57]. The yearly generation of agricultural waste in the US, particularly from corn stover and wheat straw, amounts to 215 million metric tons, whereas a majority of Europe produces more than 150 million metric tons of various agricultural wastes [58].

A rapidly developing economy, population growth, urbanization, changing lifestyles, and rising per capita energy requirements are the driving factors to India's growing energy demands. Fossil fuels account for more than 90% of the fuel needed in India, with biofuels providing an insignificant fraction. Imports meet about 85% of India's oil needs, especially for the transportation sector [59]. Domestic biofuel production offers the nation a strategic advantage because it lessens its reliance on imports of liquid fossil fuels. By investigating the market dynamics of different biofuels in India, it can be observed that bioethanol had a market value of USD 2.35 billion in 2023, which is forecast to double by 2030 [60]. Similarly, gaseous biofuels, such as biomethane and biohydrogen, had approximate market values of USD 4.20 billion and USD 1.47 billion, respectively, in India in 2024 [61,62]. Besides, there is a huge market demand for different platform biochemicals like lactic acid, succinic acid, and other organic acids derived from biomass to replace petrochemicals. Thus, the rapid innovation and development in the field of biorefinery or biofuels in India can strategically contribute to the world economy and the domestic economy. India has taken numerous initiatives to establish a strong developmental situation for biorefinery, especially for bioethanol produced from second-generation feedstocks. India is known as a global innovator in the field of bioenergy due to its rapid and effective industrial and pilot-scale programs facilitated by various governmental and nongovernmental organizations.

In 2020, Brazil and the US contributed to about 85% of the world's bioethanol production from sugarcane and corn, respectively. In contrast, India produced only 2% despite producing a huge amount of lignocellulosic residues with an annual average surplus of around 357 million metric tons, which has the potential to produce 64 billion liters of bioethanol per year and significantly lessen India's reliance on crude oil imports [56,63,64] (Figure 2). However, it should be noted that the production of bioethanol in India has steadily increased from 2057 million liters to 5300 million liters from the years 2013 to 2022, which is forecast to reach 6300 million liters by the end of 2023 [65] (Figure 3). This significant change in bioethanol production in the last 5–6 years is attributed to the facilitation of the Indian federal and provincial governments towards renewable transportation fuel [65]. The Government of India has been steadily promoting the production of second-generation bioethanol from agricultural residues to subsidize farmers and biomass producers with additional sources of income, address growing environmental concerns, and support the 20% bioethanol-blended liquid fuel program.

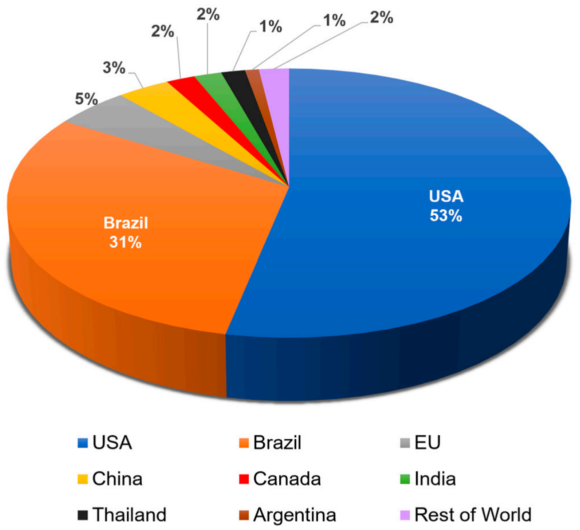

Figure 2. Major countries contributing to global bioethanol production in 2020 (Data source: Renewable Fuels Association [64]).

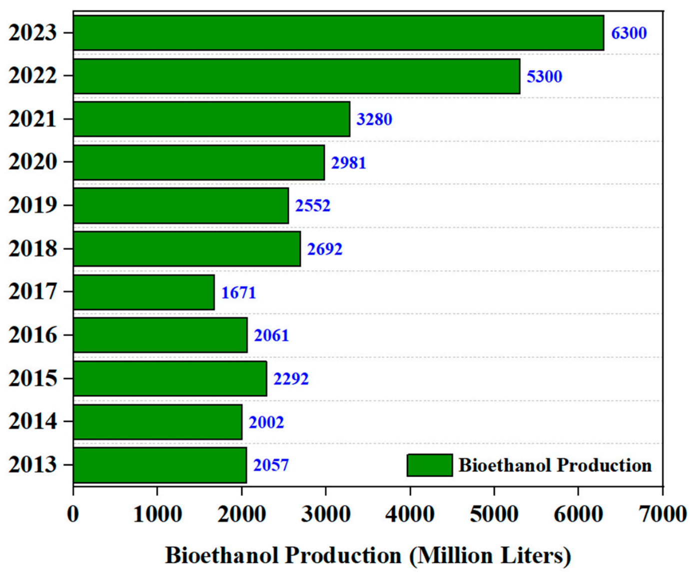

Figure 3. Bioethanol production in India over the years (Data source: Statista [65]).

Recently, some leading oil companies in India such as Hindustan Petroleum Corporation Ltd. (HPCL), Indian Oil Corporation Ltd. (IOCL), Bharat Petroleum Corporation Ltd. (BPCL), Mangalore Refinery and Petrochemicals Limited (MPCL), and Numaligarh Refinery Limited (NRL) have deliberated and strategized their plans to establish second-generation bioethanol facilities to supplement the country's growing fuel demands and accelerate the path to emission reduction. A few planned establishments of second-generation bioethanol refineries in India are shown in Table 1.

Table 1. A few proposed or planned commercial second-generation bioethanol refineries in India.

Company	Expected Plant Capacity (Kiloliters/Day)	Proposed Location
BPCL	100	Bargarh, Odisha
BPCL	100	Sagar, Madhya Pradesh
BPCL	100	Maharashtra
HPCL	100	Bathinda, Punjab
HPCL	100	Budaun, Uttar Pradesh
HPCL	100	Supaul, Bihar
HPCL	100	West Godavari, Andhra Pradesh
IOCL	100	Panipat, Haryana
IOCL	100	Gorakhpur, Uttar Pradesh
IOCL	100	Dahej, Gujarat
MRPL	60	Davangere, Karnataka
NRL	187	Numaligarh, Assam

Reference: Press Information Bureau [66]. Abbreviations: Bharat Petroleum Corporation Ltd. (BPCL), Hindustan Petroleum Corporation Ltd. (HPCL), Indian Oil Corporation Ltd. (IOCL), Mangalore Refinery and Petrochemicals Limited (MPCL) and Numaligarh Refinery Limited (NRL). Note: The authors take no liability for the accuracy of the information provided in this Table since variations in the plant capacity, location and, the proposed plans could change depending on the company's priorities, environmental approvals and other factors.

In 2019, a bamboo-based 187 kiloliters/day bioethanol refinery began operations in Assam, India, with a partnership between the Finnish biorefining company (Chempolis) in Oulu, Finland and the Numaligarh Refinery Limited in Assam, India. MRPL has started construction of a lignocellulosic bioethanol plant with an expected capacity of 60 kiloliters/day near Harihar, Davangere, Karnataka. The project has already acquired land, and in 2025, the plant is anticipated to be operational, where bioethanol will be utilized only for blending with gasoline. Besides these public sector and government-aided projects on the biorefineries, the promotion of sustainable and environmentally friendly energy sources has been significantly facilitated by the notable accomplishments in bioethanol production within the Indian business sector, particularly by known businesses such as Reliance Industries Limited, Tata Group, Adani Group, and Praj Industries Limited.

Reliance Industries Limited has been actively engaged in the production of bioethanol derived from sugarcane molasses and anticipates introducing algal biomass as a feedstock for various biofuel production, making significant contributions towards mitigating greenhouse gas emissions and fostering the use of clean energy alternatives [67]. The Tata Group has demonstrated notable progress in leveraging modern technology to produce ethanol from diverse feedstocks. Moreover, Tata Group has been a stakeholder in the BPCL project in Bargarh, Odisha, to produce 100 kiloliters/day of bioethanol [68]. Similarly, the Adani Group, which is a unicorn company dealing with petrochemicals, has determined to invest over USD 50 billion in the coming decade to create a sustainable energy ecosystem, especially focusing on bio-alcohols and biohydrogen (with a production capacity of around 1 million metric tons of hydrogen per year) [69]. This strategic move has resulted in a significant and noteworthy contribution to the biofuel industry in India. These accomplishments demonstrate the long-term vision of leading corporations to mitigate carbon emissions and advance India's renewable energy targets while promoting the utilization of bioethanol as an environmentally viable substitute for conventional fossil fuels. Significant R&D efforts on biomass conversion and biofuel applications across different academic institutions as well as public or private research organizations in India have led to these demonstration or commercial-scale interventions. The Department of Science and Technology (DST) and the Department of Biotechnology (DBT) are some of the primary funding agencies by the Government of India supporting different high-quality research projects on biofuels in addition to other fundamental, applied, and emerging areas.

According to the biorefinery policies of India, multiple feedstocks are processed by smart biorefinery techniques, which will also create a variety of outputs, including biobutanol, bioethanol, biomethane, biochemicals, and clean thermal energy. Hence, second-generation biorefineries are integrated bioenergy units, which will help address and mitigate environmental issues such as greenhouse gas emissions. Additionally, they could boost the socioeconomic growth in rural India and generate employment in the biorefinery and biomass supply chain. The generation of high-value by-products such as furfurals, xylitol, monosaccharides, organic and fatty acids, and phenolics in second-generation biorefineries has considerable potential to boost overall profitability [20,48,70].

4. Biofuel Policies and Regulations in India and Other Leading Economies

In recent years, numerous developed and developing countries have implemented several laws and policies to encourage or mandate the use of renewable energy [69]. The "Biomass Research and Development Act" became effective in the US in 2000 to effectively initiate biofuel activities [20]. Similarly, the US Environmental Protection Agency is required by law to establish production mandates for biofuels [71]. Moreover, the US government initiated the "Energy Independence and Security Act" to advance the production of biofuels for domestic energy security.

RenovaBio, a Brazilian biofuel policy, is more appealing than other programs and has led to a higher overall bioethanol blending ratio [72]. This strategy incorporates tools for lifecycle assessment, fuel market commercialization, and predictability, enhancing national energy security and reducing greenhouse gas emissions. Brazil is the only nation in the world that permits the use of E100 (100% bioethanol) in place of gasoline. In contrast, Sweden is the only country that utilizes E85 (85% bioethanol blending with gasoline) and has the highest usage of biofuels (up to 32%) in Europe. The German "Biofuel Quota Act" of 2007 recommended a 17% target for biofuels by 2020 [73]. The UK follows an E5 mandate (5% ethanol blending), which is a lower blending ratio compared to other countries.

The Government of China unveiled laws in September 2017 that mandate the use of bioethanol with a 10% bioethanol blend target in fuel for the entirety of China [74]. In Thailand, the "Alternative Energy Development Plan" aims to boost the proportion of renewable and alternative fuels from 7% of total fuel energy usage in 2015 to 25% in 2036 [20,59]. New Zealand, Australia, Colombia, Bolivia, Peru, Malaysia, the UK, Paraguay, the Philippines, South Korea, and South Africa have proposed to implement mandates on the percentage of biofuel blends [75–77].

To meet its escalating needs for transportation fuels, India largely relies on importing petroleum crude from Russia and a few Gulf countries. Since 2003, the Government of India has started E5 (5% bioethanol) blending with gasoline in four union territories and nine states, which was later extended to 20 states by 2006 [78]. The "National Mission on Biodiesel", which sought to reach 20% biodiesel blending in petrodiesel by 2012, was introduced together with the adoption of the biofuel mission in 2003. Moreover, the "National Policy on Biofuel", first released in 2009, was amended twice in 2018 and 2022. The goal of this policy is to lessen the dependency on imports of petroleum products by promoting the development and production of biofuels domestically. The National Policy on Biofuels 2009 projected an optional 20% blending goal for bioethanol and biodiesel by 2017. It aimed to promote the best indigenous biomass feedstock growth for biofuel production. It provided a framework for allowing technological, institutional, and financial initiatives that outlined the vision, objectives, and plan for producing biofuels.

The "National Mission on Biodiesel" by the Government of India started in 2003, where the primary recommendation made by the government was to grow Jatropha on 11 million hectares of wasteland by 2012. However, the government's goals were hampered due to the higher cost of biodiesel production than its purchase price [79]. Additionally, the National Mission on Biodiesel lost traction and interest due to numerous economic and agronomic restrictions. Although most of the local administrations have kept the state excise tax in place, one financial incentive for biodiesel production was the exemption from the 4% central excise tax.

In 2018, the new National Policy on Biofuels by the Government of India became effective, which recommended a blending target of 5% biodiesel in diesel and 20% bioethanol in gasoline by 2030 [80]. Reduced imports of crude oil, increased farmer income, rural jobs, optimum use of drylands, and environmental sustainability are the major objectives of the new National Policy on Biofuels. This policy was also commissioned to provide financial and tax advantages tailored to the first-, second-, and third-generation biofuels. However, this policy was modified by the Indian Union Government in 2021–2022 to set the goals for bioethanol blending for 2025. Additionally, the use of residual food grains or food waste generated from the different food processing units, such as surplus corn and rice, was permitted as the feedstocks to generate biofuels. According to the recently formed expert committee on the "Roadmap for Bioethanol Blending in India", 14 billion liters of bioethanol are expected to be produced by 2025 to meet the updated targets [81,82]. The plan aims to produce 6.8 billion liters of bioethanol from sugarcane and 6.6 billion liters from food grains, which poses a significant impact on the agriculture sector.

The Government of India accelerated its E20 goal to blend 20% bioethanol into gasoline by 2025, five years earlier than it was planned to be executed [82]. However, the deficit of bioethanol is a major challenge to achieving this target. To meet the 10% bioethanol blending objective, about 4.5 billion liters of bioethanol will be required, considering the demand for gasoline by 2022 [20]. However, the existing production capacity, which mostly relies on bioethanol derived from first-generation technologies, is insufficient to meet 10% blending standards. The "JI-VAN" (Jaiv Indhan-Vatavaran Anukool Fasal Awashesh Nivaran—in Hindi) initiative was established by the Government of India's Ministry of Petroleum and Natural Gas in 2017 to provide financial assistance to lignocellulosic (second-generation) biorefineries [9]. The global expansion of biorefineries has been accelerated by these policies, which have encouraged the efficient use of plentiful lignocellulosic biomass for the sustainable production of by-products.

5. Challenges for Commercialization of Second-Generation Biorefineries

5.1. Supply Chain and Availability of Second-Generation Biomass

The potential obstacles for second-generation biorefinery operations are illustrated in Figure 4. Despite the higher initial investment required, biorefining proves to be a more economically efficient approach. Therefore, to ensure economic feasibility, the feedstock utilized in the biorefinery must be both cost-effective and readily accessible [19]. Various categories of second-generation biomasses can be used as feedstock, contingent upon their availability at different times throughout the year. Nevertheless, the main challenge in the commercialization of second-generation biorefineries is the consistent affordability of seasonal feedstock [83]. Considerable amounts of agricultural residues are generated in Asian countries such as China and India, presenting a viable opportunity for utilization as feedstock in biorefineries. According to a report by Datta et al. [84], India produced over 685 million metric tons of agricultural waste in 2018. However, a significant portion of this trash, up to 87 million metric tons, was disposed of by open burning on the farm, which consistently led to poor regional air quality and smog formation lingering for several days.

The primary source of raw materials for biorefineries consists of the surplus biomass available within a specific nation. For instance, Canada's predominant source of lignocellulosic biomass is derived from forest wastes since it contains 9% of the world's forests, resulting in an annual production of around 52 billion liters of biofuels, primarily as bioethanol [20]. As a result of the considerable availability of these sustainable biomass resources, countries such as the US and Brazil employ the residual corn stover and sugarcane bagasse. Furthermore, several biorefineries in the US rely on dedicated energy crops (e.g., switchgrass, elephant grass, hybrid poplar, etc.) as supplementary sources of second-generation feedstock due to their fast growth cycle, less-intensive cultivation practices, and high biomass yield [70]. Within the European Union, a variety of biomass sources originating from forestry, fishery, and agriculture are employed to generate biomaterials and bioenergy [77].

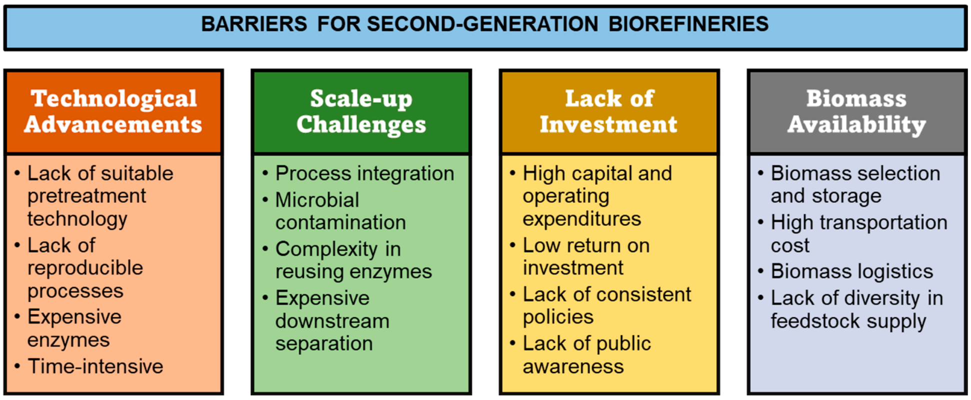

Figure 4. Potential challenges in the commercialization of second-generation biorefineries.

The determination of the minimum selling price for second-generation feedstocks in a biorefinery at a certain site is heavily influenced by the expenses associated with purchasing biomass from farmers as well as the costs incurred during its bulk transportation and storage. Hence, it is imperative to assess the financial implications associated with the preprocessing and postprocessing stages of biomass before proposing the establishment of a biorefinery. Furthermore, it has been observed that the expenditure on feedstock in second-generation biorefineries constitutes around 50% of the total production cost of bioethanol [85]. Various types of biomasses can be utilized to address this issue, enabling uninterrupted availability of biomass resources at a single site throughout the year. To ensure the sustainable operation of biorefineries, the concept must incorporate facilities for the utilization of diverse feedstocks, hence mitigating dependence on a particular variety of biomass [47]. The various stages involved in the supply chain of a biorefinery's feedstock encompass sorting, transportation, storage, and biomass processing [86]. The primary factor influencing the minimum selling price of the feedstock logistic network is predominantly the transportation expenses.

According to Usmani et al. [20], the expenses related to the large-scale production of biofuels can vary between 40% and 60%, encompassing factors such as supply chain management and feedstock processing. The determination of biomass transit and storage duration is contingent upon the geographical establishment of the biorefinery. To mitigate the increased final minimum selling price and transportation expenses associated with feedstocks, the proximity of the feedstock availability to the biorefinery must be ensured [87]. Potential options for outlining the feedstock supply chain include the development of biomass exchange models that can effectively meet both economic and environmental criteria, as well as the use of biomass torrefaction and densification techniques to reduce volume [86]. The moisture content, expressed as a percentage, is a significant concern about the storage and transportation of biomass. Microbial growth within the moisture content range of 20% and above has the potential to affect both the biomass composition and selection of the conversion process. In addition, another barrier is the task of maintaining an equilibrium between the demand and supply of biomass to establish a steady bioresource market. The presence of competition among suppliers in the biomass market has the potential to mitigate fluctuations in prices.

5.2. Efficiency of Pretreatment and Enzymatic Saccharification

Along with the availability of biomass and the supply chain, choosing an effective pretreatment method for different feedstocks is a crucial challenge that must be taken into consideration. Biomass pretreatment is considered an essential step in the effective usage of second-generation biomass because it disintegrates the structure of biomass and separates the cellulose hemicellulose from the lignin matrix [17]. Furthermore, it improves the efficiency of the final products followed by subsequent saccharification and fermentation processes. Several physicals (e.g., extrusion and milling), physicochemical (e.g., steam explosion and ammonia fiber expansion), chemical (e.g., alkalis, acids, and ionic liquids), and biological (e.g., bacteria, fungi, and enzymes) pretreatment methods have been developed for effective biomass pretreatment and hydrolysis [13,19,20].

Table 2 lists the benefits and drawbacks of a few biomass pretreatment technologies. A significant problem in second-generation biomass pretreatment is the formation of high-solid loadings. Therefore, for easier processing, increased production and productivity and efficient feeding of biomass into various reactors with a high total solid concentration is crucial. Additionally, the economics of the process can be enhanced by recovering and reusing the chemicals and enzymes used in any pretreatment procedure.

Table 2. Comparison of second-generation biomass pretreatment methods.

Methods	Mechanism	Advantages	Disadvantages
Biological pretreatment			
• Enzymes (laccases, peroxidases, etc.) • Microorganisms (fungi and bacteria)	• Decomposition of polysaccharides to monosaccharides.	• Low energy intake • Requires no chemicals • Mild reaction conditions	• Lower hydrolysis • Slower process • Continual monitoring is required to prevent contamination
Chemical pretreatment			
• Organosolv method • Dilute sulfuric acid • Alkali bleaching • Ionic liquid • Deep eutectic solvents	• Releasing of lignin and/or hemicellulose increases the accessible surface area of cellulose.	• Moderate reaction rates • Higher yield of sugars • High delignification efficiency • High conversion rate	• Corrosive, toxic and hazardous material handling is required • More water is required • High amounts of wastewater are generated • Loss of lignin and hemicellulose is inevitable
Physicochemical pretreatment			
• Torrefaction • Ammonia fiber expansion • Steam explosion • Wet oxidation	• The breakdown of biomass cell walls increases the digestibility of fibrillated cellulose • Drying of biomass enhances bulk handling and storage	• Less corrosive chemicals are involved • Highly effective	• Cost-effective setup • Require special reactors • Require high pressures and temperatures

Pretreatment is often expensive and essential, accounting for roughly 30–50% of the cost of all equipment and 20–25% of all operational costs in second-generation biorefinery [20,48]. Compared to the physical pretreatments, the chemical pretreatment method uses less energy. However, the use of different chemicals and certain digesters makes the process more expensive [88,89]. The chemical reactions result in the production of toxic or inhibitory products (e.g., furfurals, organic acids, and phenolics), which need to be neutralized before saccharification and fermentation [90]. Several researchers have suggested using techniques such as membrane evaporation, biochar-based adsorption, and ionic liquid-based pretreatment to remove inhibitors continuously while boosting production [14,47,88,91].

In biological pretreatment, microorganisms and their hydrolytic enzymes are utilized to break down the structure of cellulose and hemicellulose into monomeric pentose and hexose sugars [40–42]. Recently, biological pretreatment processes have been adopted over other pretreatment methods due to their low energy consumption, non-toxic by-product formation, and environmental friendliness [92]. However, the slow rate of microbial growth and expensive enzymes are some key challenges in the biological pretreatment of biomass.

The following pretreatment requirements are anticipated for successful commercialization of the second-generation biorefineries: (i) avoiding severity in biomass pretreatment conditions, (ii) reducing the formation of toxic or inhibitory by-products, (iii) preventing the loss of hemicellulose sugars, (iv) ensuring less water and energy consumption, (v) seeking valorization of lignin, (vi) cost-effective recycling of catalysts, and (vii) seeking total utilization of by-products for a closed-loop and circular bioprocessing approach.

As mentioned earlier, upon biological pretreatment, the polysaccharides undergo enzymatic hydrolysis to yield monosaccharides. The expenses associated with enzymatic hydrolysis can constitute around 25% of the overall expenditures in a second-generation biorefinery [9,20]. Therefore, it is of utmost importance to develop cost-effective enzyme combinations for the conversion of second-generation biomass into the desired products. The efficacy of enzymatic hydrolysis is impacted by various factors, including catalytic parameters, enzyme loading, hydrolysis duration, temperature, and pH [93–95]. Different pretreatment approaches result in a diverse composition of biomass, necessitating the adoption of a tailored enzymatic combination for each unique biomass. On-site enzyme manufacturing technology has recently been proposed as an alternative to conventional off-site enzyme production facilities to reduce the price of hydrolytic enzymes [96].

Several studies have examined the issues associated with scaling up, particularly in the context of second-generation biorefineries. These studies have suggested that an integrated approach to enzyme production is a recommended method [97–99]. When second-generation biomass is utilized for both enzyme production and enzymatic hydrolysis, microorganisms can generate enzyme isoforms that exhibit enhanced substrate affinities [100]. Consequently, market players involved in the production of enzyme combinations should be attracted to this area to facilitate the cultivation of specific fungal strains capable of synthesizing biomass-specific enzymes. Research efforts should be invested to engineer microorganisms capable of efficiently fermenting and hydrolyzing pretreated or minimally treated lignocellulosic biomass at levels of productivity that are adequate for industrial applications [101–103].

5.3. Technology Scale-Up

The process of scaling up second-generation biorefineries to meet the increasing need for renewable energy products presents considerable challenges. In many cases, the parameters and operational conditions that have been adjusted at the laboratory scale may not exhibit the same level of efficiency when applied to demonstration-scale or pilot-scale operations [70,99]. The identification of pertinent factors for transitioning from laboratory-scale to pilot-scale, and subsequently to commercial-scale is of utmost importance. Several important factors need to be considered when scaling up biorefineries for commercialization, including the development of techno-economic models, process optimization, technological advancements, lifecycle analysis, and the simulation of cost and risk mitigation [77,104,105]. Furthermore, it is important to consider several other essential factors, such as minimizing waste discharge streams, limiting water consumption, efficiently utilizing resources (biomass, materials, equipment, and labor), appropriately integrating pretreatment and conversion techniques, diversifying products for the expansion of second-generation biorefineries [106].

The sequence of expenses in biomass management and processing involves prioritizing operational expenditures followed by capital expenditures, as the latter determines the approach for scaling up operations. To mitigate the risk of a commercial failure, it is imperative to safeguard capital expenditures and actively seek opportunities to minimize it to the greatest extent possible. One potential strategy for reducing the initial expenses involved with establishing a greenfield site is to leverage the existing infrastructure within enterprises engaged in the production of biochemicals [20].

It is also essential to consider the automation of second-generation biorefinery operations for effective commercialization. Automation can eliminate manual interventions, enhance operational efficiencies, and reduce energy use [48,95]. The implementation of second-generation bioethanol facilities in future production is imperative due to several factors. These include the substantial production costs associated with such facilities, significant political and regulatory problems surrounding their establishment, as well as the technological hazards they provide, and their limited potential returns.

Besides automating the conversion processes, another major step can be taken in the commercialization of second-generation biofuels, which is the establishment of an integrated, flexible, and versatile conversion process. Unlike the "single product" biorefinery approach, the integrated biorefinery approach works in synergy to combine biological and thermochemical conversion processes to utilize resources and by-products and manage wastes to deliver multiple products. The commercialization of the integrated biorefinery process appears to be more attractive, feasible, and sustainable. For instance, in a bioethanol refinery, a major by-product is CO_2 resulting from microbial metabolism, which can be reused as a non-polar solvent by converting it into supercritical CO_2 fluid that can be used as an environmentally friendly extraction medium for food-grade extractions. Moreover, the major problem in a commercial bioethanol plant relies on the utilization of the residual or spent feedstock generated from the bioethanol making can be used as the feedstock for the production of carbon-rich bioproducts (e.g., biochar, hydrochar, and activated carbon) through the carbonization of the residual biomass, which can be used as a solid fuel that can be used in the distillers to for energy or can be used as a fertilizer in agriculture. This integration of the different bioconversion processes will feasibly achieve the commercial bioethanol refineries by establishing a multiproduct and zero-waste approach.

6. Future Prospects and Recommendations

Table 3 presents the strengths, weaknesses, opportunities, and threats (SWOT) analysis of the second-generation biorefinery, which is intended to guide its future development. There is a wide availability of processing technologies and valorization strategies for mixed biomass in the context of second-generation biorefinery. The scaling-up process of two biorefineries poses a significant barrier in terms of their commercialization. Therefore, drawing from the findings of laboratory and pilot-scale investigations, it is imperative to establish a complete repository of second-generation biomass treatment techniques and their corresponding process optimization strategies. The establishment of a second-generation biorefinery setup with high efficiency and scalability would yield significant advantages.

The utilization of state-of-the-art biotechnological methods and novel single-step technologies is imperative to achieve cost competitiveness with fossil fuels driven by the progress made in second-generation biorefinery. Accordingly, it is possible to provide an extra research platform that facilitates the integration of second-generation biorefineries with existing petroleum refineries, thus enabling sustainable applications. The primary objectives of the integrated biorefinery model are two-fold: (i) to optimize the utilization of second-generation biomass by simultaneously producing biofuels and value-added biochemicals, and (ii) to integrate two biorefineries with an existing petroleum refinery to reduce both initial investment and ongoing operational expenses [77]. Hence, it is reasonable to prioritize this viewpoint considering the progressively diminishing large-scale use of fossil fuels.

Table 3. SWOT analysis of second-generation biorefinery for future development.

Strengths	Weaknesses
• Sustainable development of energy and products, carbon-neutral and eco-friendly • Circular bioeconomy concept • Less reliance on fossil fuels • Waste management and minimization • Open to agricultural and chemical processing sectors for collaboration • Boosts rural economy and generates additional revenue sources for industries and individuals	• Higher operational and capital expenses • Lack of funding for operations at a commercial scale and demonstration • Distinctive gap among lab-scale, pilot-scale, and commercial-scale processing • Lack of uniform biomass supply chain • Difficulty in large-scale biomass processing
Opportunities	**Threats**
• Strengthening of the economy by clustering of agricultural, chemical, and energy sectors • Increase employment opportunities • Scope to reduce greenhouse gas emissions • Generation of technical and scientific knowledge base • Ensures domestic energy security • Innovation for waste to energy • Increased creation of start-up and spin-off companies	• Consistent use of traditional energy sources (e.g., fossil fuels) is a major threat. • Dwindling investments due to long-term uncertainty and risks • Inconsistencies relating to seasonal biomass availability and logistical difficulties • Immaturity in process improvement and automation • Food-versus-fuel debate

References: Usmani et al. [20], Singh et al. [48], Chandel et al. [70].

It is worth noting that second-generation biorefineries have the potential to utilize alternative methodologies that differ from the infrastructure often applied in petroleum-based refineries. To ensure a circular economy, the residual or discarded second-generation biomass can be utilized to generate syngas, value-added products, and long-chain hydrocarbons within refineries [107,108]. Therefore, this has the potential to enable the utilization of diverse feedstocks more efficiently, resulting in the production of many co-products including power and heat. The utilization of lignin, a residual substance with a high energy density, can also be employed for energy production.

7. Conclusions

The second-generation biorefinery has gained attention due to environmental concerns, the growing need for energy, and global warming. This has led to increased interest in the production of bioethanol, which can be used as a commercial and sustainable biofuel and industrial biochemical. The development of second-generation biorefinery offers numerous advantages. Nevertheless, the commercialization of biofuels and valuable chemicals poses significant challenges, encompassing the consistent availability of feedstock, the technological intricacies of the conversion process, and the imperative of cost-effectiveness for scale-up. Therefore, the implementation of second-generation biorefinery necessitates the establishment of a more robust supply chain that would effectively utilize the surplus lignocellulosic biomass into biofuels and biochemicals. Brazil has proposed a 100% (E100) blending of bioethanol, while India amended its biofuel policies to meet a target of 20% (E20) bioethanol blending in the near future. On the other hand, countries like the US, Russia, Germany, China, and the Gulf countries have targeted a bioethanol blending of 5–17%. In addition, to achieve this blending of E20, India (in association with leading oil corporations and established for-profit organizations) has established a few bioethanol refineries across its subcontinent using abundantly available lignocellulosic feedstocks such as rice husk, wheat straw, corn stover, and other agricultural biomass by implementing various advanced fermentative and effective pretreatment techniques.

To effectively maximize and maintain the potential of a second-generation biorefinery, it is necessary to amend government policies on biofuels in regular intervals, ensure the availability of biomass throughout different seasons, make advancements in technology for biomass processing and pretreatment, develop indigenous enzyme cocktails, and value-addition of the by-products that are suitable for various types of lignocellulosic biomass. Moreover, biofuels have the potential to serve as sustainable and environmentally friendly energy sources when employed responsibly. This could lead to a multitude of advantageous consequences encompassing the transformation of waste into valuable resources, enhancement of energy stability, mitigation of carbon emissions, use of impaired and unutilized food grains, augmentation of agricultural income, generation of employment chances, and expansion of avenues for investment.

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