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TRANSFORMATION OF SOLID WASTE INTO RENEWABLE ENERGY: PERSPECTIVES FOR THE PRODUCTION OF 2G BIOFUELS

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ABSTRACT

Turning residual biomass into bioenergy promotes rational environmental waste disposal and turn it into a source of energy. In the last decade, the idea of using lignocellulosic biomass to make second-generation (2G) biofuels has become more popular in the energy industry. Thus, this study aimed to show the potential of residual lignocellulosic biomass as raw material for clean and sustainable energy and the technological advances focused on making it economically viable. A narrative review was adopted, in which the material used in the bibliographic survey was organized from scientific sources collected in high-relevance databases. The various factors presented in the review guarantee that the use of lignocellulosic biomass is considered a promising substrate. Furthermore, it indicates a solution to the competition between food supply and fuel production, which occurs with first-generation biofuels, which in the long term seem to be unsustainable. However, despite technological advances for its production and commercialization on a large scale, investment in scientific research is necessary to make the adopted technologies viable.

INTRODUCTION

The rapid increase in energy consumption and human dependence on fossil fuels has led to the accumulation of greenhouse gases (GHGs) and, therefore, climate change. Thus, clean renewable fuel alternatives must be developed, tested, and adopted. Moreover, significant efforts need to be dedicated not only to overcoming technological barriers, but also to integrating social, economic, and environmental factors to provide long-term, economical, and reliable production systems for the biofuel industry (Liu et al., 2021).

Biofuel technology has evolved through several generations of significant advancements. The predominant issue with first-generation biofuels is that they are derived from food crops (e.g., corn and sugar cane), which require fertilization, water, and soil and therefore compete directly with food production (Liu et al., 2021). To mitigate the food vs fuel debate, renewable feedstocks such as lignocellulosic

biomass are explored as alternatives for second-generation biofuel production (Nanda et al., 2019).

Lignocellulosic materials, despite being among the largest biomasses generated in the world, are still underutilized (Pacheco & Silva, 2019). This type of raw material is composed of different polymers such as polysaccharides (cellulose and hemicellulose), phenol aldehyde polymer (lignin), along with interwoven polar and nonpolar substances (Chen et al., 2017). Therefore, it has a complex, highly crystalline, and chemically bonded structure built to withstand environmental conditions and consequent resistance to biodegradation (Krasznai et al., 2018).

Biofuel production from lignocellulosic biomass depends on the microbial conversion of sugars and cell wall components into fuels and desired products (Perez-Pimienta et al., 2019). However, the recalcitrance of raw materials is a major bottleneck for process viability and may affect its future commercialization. Adequate access to polymers is only possible through appropriate pretreatment, but these

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methods require high cost and energy consumption (Amin et al., 2017; Santos et al., 2019). These techniques aim to deconstruct the lignocellulose structure by breaking the chemical bonds present in biomass, which in turn increases access of enzymes to the material to convert it into desired biofuels and biochemicals (Mahmood et al., 2019).

Despite being a major contributor to the recalcitrance of the feedstock, lignin is also a promising substrate for specialized microorganisms that can convert these aromatic polymers into usable products (Fang et al., 2020). Currently, fossil fuels are produced at a much lower cost than biofuels. Thus, simultaneously producing value-added products along with second-generation biofuels through the incorporation of metabolic pathways would increase the economic viability of the process (Yang et al., 2020). Technological progress has been significant in producing lignocellulosic biofuel, making it a clean and economically viable process, including advances in energy crop engineering strategies, efficient lignocellulose degradation, and simultaneous production of high-value products (Liu et al., 2021).

Given the above, this review aimed to address the potential of lignocellulosic biomass from agro-industrial waste for the production of 2G biofuel, highlighting the main advances and challenges for it to become a commercial reality.

REVIEW

Our review aimed to examine the potential of lignocellulosic biomass from agro-industrial waste for producing second-generation biofuels by discussing the main advancements and challenges toward its commercial feasibility. The method applied was narrative analysis, which described and discussed the topic of “Converting solid waste into renewable energy: perspectives for 2G biofuel production” from a scientific, theoretical, and contextual viewpoint. The literature search was conducted using the Web of Science, Scopus, and Science Direct databases, which were considered relevant sources of peer-reviewed abstracts and citations. The search was performed using a combination of keywords such as “lignocellulosic biofuel,” “lignocellulosic wastes for biofuel production,” and “biofuel 2G” in the title, abstract, or keywords of the articles. English was used as the standard language in all databases to increase the search spectrum of the studies.

Lignocellulosic biomass

The biofuels and biochemicals derived from lignocellulosic biomass have emerged as clean products to complement fossil-based resources and reduce environmental impacts. This lignocellulosic biomass is considered a renewable, cheap, and abundant resource for producing a wide variety of liquid, gaseous and solid biofuels, and industrially relevant biochemicals. Different conversion technologies (biological conversions like fermentation and anaerobic digestion), thermochemical (liquefaction, gasification, and pyrolysis), and catalytic (transesterification) can be used to produce fuel and chemicals from this type of feedstock (Okolie et al., 2021).

The main sources of lignocellulosic biomass are forest waste, agricultural waste, energy crops, organic solid urban waste, and industrial waste such as wood, paper, and cellulose (Roy et al., 2021). Its composition is diverse, with

a complex structure consisting mainly of cellulose (40-60%), hemicellulose (20-40%), and lignin (10-25%) along with other minor components like minerals, acetyl, and phenolic groups. The crystallinity of cellulose, hydrophobicity of lignin, and the way lignin and hemicellulose are strongly bonded together by covalent and hydrogen bonds make the material strong and resistant (Woiciechowski et al., 2020). Cellulose is a glucose polymer consisting of D-glucose subunits linked by β -1,4, while hemicellulose includes pentose and hexose sugars (Nanda et al., 2015). Lignin, in turn, is a phenylpropane polymer bonded by ester links and acts as an adhesive binding cellulose and hemicellulose (Fougere et al., 2016).

However, because of their heterogeneous structures, lignocellulosic materials face limitations in their valorization, such as the difficulty of substrate saccharification or hydrolysis by enzymes (Ashokkumar et al., 2022). To resist microbial and enzymatic deconstruction, lignocellulose has complex structural and chemical mechanisms, providing natural resistance, known as biomass recalcitrance (Himmel et al., 2007). Thus, an effective pretreatment technology is necessary to break down its complex structure and produce the desired value-added bioproducts (Yiin et al., 2021).

Lignin is removed by pretreatment techniques, whether physical, chemical, or biological, which helps modify biomass structure, facilitating hydrolysis to obtain a high process yield (Mankar et al., 2021). Biological and thermochemical routes are the two main ways to convert biomass into biofuels and biochemicals (Parakh et al., 2020). Biological routes, such as anaerobic digestion and fermentation, use microorganisms and enzymes to break down biomass into green fuels and chemicals. On the other hand, heat and chemical processes are used in the thermochemical route to break down biomass into fuels and sustainable chemicals (Cai et al., 2017). Examples of thermochemical routes include pyrolysis (Azargohar et al., 2014), gasification (Azargohar et al., 2019), liquefaction (Chand et al., 2019), and carbonization (Kang et al., 2019).

A proper transformation of lignocellulosic materials is essential for lignocellulosic biomass-use efficiency and economic, eco-friendly, sustainable processes in lignocellulosic biorefineries (Chuetor et al., 2021). Lignocellulosic biomass-based biorefineries have recently emerged as promising due to their potential reuse of biomass in various industrial bioproducts, including renewable resources (Abraham et al., 2020) in addition to other value-added products such as organic acids, polyhydroxyalkanoates (PHA), biochemicals, and bioplastics at competitive prices (Usmani et al., 2021). In this context, high-purity lignin gains relevance in applications with higher polymer value, such as the production of nanoparticles for the bio-composites sector, which, in turn, increases process profitability (Tian et al., 2017). More than 200 value-added compounds can be generated by processing lignocellulosic material through various treatment techniques (Isikgor & Becer, 2015).

Pretreatments

Lignocellulosic biomass pretreatment is a crucial step for several purposes, such as: (i) altering the lignocellulosic structure and obtaining individual constituents, (ii) producing high reactivity in the material for later application, and (iii) preserving the initial forms of

lignocellulosic constituents (Bhatia et al., 2020). It must consider several challenges, including cost reduction, environmental concerns, and sustainability. Moreover, as its efficiency is affected by many physical and chemical factors, such as lignin content, cellulose crystallinity, and specific surface area, a single method does not provide the desired degradability. Therefore, some methods should be combined to improve process efficiency (Ashokkumar et al., 2022).

During pretreatment, lignocellulosic biomass is degraded into fibrous components, increasing the rate of chemical reactions, and heat and mass transfer in the following biochemical conversion into higher value-added products, such as biochemicals and biofuels. To this end, several methods have been explored to find the one that best converts lignocellulosic biomass, both in terms of efficiency and cost-effectiveness (Ab Rasid et al., 2021).

Each biomass pretreatment type can be done using different techniques that can have varying effects. Most physical and chemical pretreatments use mechanical grinding, irradiation, acids or bases, steam explosion, or combined processes that require high energy (steam and electricity) and corrosion-resistant high-pressure reactors. Additionally, the various inhibitors produced during pretreatment with traditional approaches significantly affect enzymatic hydrolysis or fermentation yields (Kumari & Singh, 2018).

A sustainable pretreatment should meet certain criteria, such as efficient alteration of cellulose for the enzymatic attack, minimal loss of hemicelluloses and cellulose, no or less generation of inhibitors, low energy requirements, low cost for reducing biomass size and reactors, no or low formation of waste, and low or no chemical product consumption (Gupta & Verma, 2015). In this sense, biological pretreatment could present significant potential in meeting most of these sustainable criteria (Saha et al., 2017).

Biological pretreatments (BP) are usually done by growing microorganisms directly on biomass or using enzyme cocktails (Ummalyma et al., 2019). BP with fungi can be used to eliminate some inhibitors generated by other lignocellulosic pretreatments (Zanellati et al., 2021). Some enzymes are capable of pretreating lignocellulosic material, such as cellulases, hemicellulases, ligninases, and pectinases (Ummalyma et al., 2019). Thus, BP can be categorized into microbial pretreatment (fungal, bacterial, microbial consortium, and ensilage) and enzyme pretreatment and is a safe and eco-friendly method for removing lignin from lignocellulose. However, industrial adoption is still rare for lignocellulosic biomass due to large limitations involving costs and environmental concerns (Sindhu et al., 2016).

Physical pretreatment technologies aim to alter the partial physical and chemical properties of the lignocellulosic biomass, such as the cellulose crystallinity, degree of polymerization, and specific surface area. Reducing the size of lignocellulosic biomass through mechanical means, radiation, ultrasonics, and electron beams are the most well-known and used physical methods. The mechanical reduction of size involves decreasing the particle size through breaking, grinding, or pulverization by destroying the microstructural voids in the material (Chuetor et al., 2017).

Chemical methods come in various techniques that use acids, bases, ionic liquids, organic solvents, and deep

eutectic solvents. Acid pretreatment involves the use of inorganic acids, including H_2SO_4 , H_3PO_4 , HNO_3 , and HCl , or organic acids such as CH_3COOH , formic acid, maleic acid, and oxalic acid (Jędrzejczyk et al., 2019). A comparison of different chemical pretreatments showed that 2% (v/v) diluted acid (H_2SO_4) could remove around 80.2% of lignin (Nazli et al., 2021). However, using diluted and concentrated acid causes significantly low solid recovery. Recycling the used acid solution is still being explored for an economical value-adding fractionation process of lignocellulosic materials (Ashokkumar et al., 2022).

The main basic reagents used for lignocellulosic alkaline pretreatment are NaOH , KOH , and $\text{Ca}(\text{OH})_2$, which can be performed at a temperature of 90-160°C (Kim et al., 2016). However, alkaline pretreatment causes several problems, mainly the generation of black liquor (an aqueous solution of lignin residues, hemicellulose, and the inorganic chemical used in the process) and high energy consumption for hydrolysis (Vu et al., 2020). In addition to sustainability, combining alkaline pretreatment with other methods, such as mechanochemical-assisted alkaline, can improve the reactivity of lignocellulosic material and increase the yield of fermentable sugar (Shen et al., 2020).

Organic solvent pretreatment is considered a promising technique that uses ethanol, methanol, acetone, glycols or phenols, and small amounts of acids (H_2SO_4 or HCl) to enhance the efficiency of pretreatment (Capolupo & Faraco, 2016). For example, the effect of this pretreatment using acetone and an acid catalyst (H_2SO_4) in an autoclave at a constant temperature of 121 °C resulted in a yield of 80% glucose (Singh et al., 2022).

Pretreatment with ionic liquids is used to dissolve cellulose and lignin in complex lignocellulosic material by cleaving hydrogen bonds in the material by forming hydrogen bonds with sugar hydroxyl groups. Two different ionic liquids, calcium lysinate, and ethanolamine acetate, in enzyme hydrolysis and ethanol fermentation of various kinds of wood, can produce significant percentages of glucose (24-84%) and xylose (14-80%) (Das et al., 2021).

Another chemical process that is attracting a lot of attention and is considered a green solvent for lignocellulosic pretreatment is deep eutectic solvents (DESs) (Ashokkumar et al., 2022). DESs are a special mixture of two components: hydrogen bond donor and hydrogen bond acceptor (Abbott et al., 2003). The efficiency of this pretreatment combined with thermal bamboo deep eutectic solvents in the presence of choline chloride and the lactic acid at 140°C for 6 hours reached 80.1% delignification with 99.49% purity. The use of DES pretreatment is favorable for producing cellulose nanofibrils from lignocellulosic biomass, removing amorphous cellulose and non-cellulosic components (Yu et al., 2020). However, the disadvantage of using deep eutectic solvents and ionic liquid treatment methods on an industrial scale is the high initial cost of solvents, but this can be amortized in a long-term operation. The cost could be reduced since they are biodegradable and easily recycled (Ab Rasid et al., 2021).

Other green pretreatment methods like ozonolysis and steam explosion have also proven to be safe, environmentally friendly, and economically feasible, especially for biofuel production. Among these, steam explosion has been reported as one of the most effective, as it not only obtains high yields of fermentable sugars but also does not consume chemical reagents, using a closed-loop,

non-toxic reagent recycling system and thus reducing environmental pollution (Ab Rasid et al., 2021). While ozonolysis pretreatment is effective and consumes zero chemical reagents, the high energy input required for ozone production has been a major concern for industrial use; therefore, more studies are needed to redesign the ozone generation system to minimize energy consumption and reduce costs (Ab Rasid et al., 2021).

Since different lignocellulosic biomasses have different characteristics and compositions, it cannot be concluded that one pretreatment method is the most efficient for all types. The efficiency of lignocellulosic biomass pretreatment method varies depending on the biomass composition, chemical reaction with the solvent, type of reactor, and other operational parameters. The future application of green pretreatment systems has been greatly improved by new technologies with promising results, but there is still room for improvement. More studies need to be done to expand and develop these methods so they can be integrated into industrial-scale production, aiming to reduce production costs (Ab Rasid et al., 2021).

Major 2G Biofuels

Biodiesel

Biodiesel is produced in larger amounts from vegetable oils and animal fats and is a sustainable option (Jayakumar et al., 2021). These sources are abundant, making biodiesel readily available (Yin et al., 2020). Biodiesel is referred to as monoesters of fatty acids and is produced by the transesterification of triglycerides and esterification of free fatty acids with alcohol (Jambulingam et al., 2020). The raw materials used for second-generation biodiesel production mainly include non-edible oils, kitchen waste oils, and animal fats (Ziolkowska, 2020).

Biodiesel can be used as a drop-in fuel (Shiu et al., 2010). Drop-in biofuels can be mixed with conventional diesel to a specific ratio and can be used with the existing fueling infrastructure, without the need for adaptation (Pires et al., 2018). The transesterification process can be improved using different types of catalysts (Nasreen et al., 2018). The catalysts used in the transesterification of oils and fats for biodiesel can be acids, bases, or enzymes (Reddy et al., 2018).

The chemical catalyst method of producing biodiesel is currently the dominant method on a large scale using virgin oils due to high conversion rates and lower operational costs (Amini et al., 2017). The diverse composition of oils/fats requires investigations into the best catalysts for efficient biodiesel synthesis. Chemical catalysts, mainly made of acids (H_2SO_4 , BF_3 , H_3PO_4) and bases (KOH, NaOH), are used industrially in biodiesel production. Bases, although cheaper and faster, are suitable for raw materials with less than 0.5% by weight of free fatty acids (FFA), while acids require lower water content with raw materials mainly rich in FFA such as used cooking oils. These drawbacks are associated with high-temperature requirements, extensive product washing, and plant corrosion, which can be avoided when lipases are used (Ruhul et al., 2015; Falizi et al., 2019).

Therefore, the production of biodiesel has inherent problems associated with the primary raw materials and chemical catalysts used (Moazeni et al., 2019). In this scenario, enzymes, which are bio-chemical catalysts, can be

used in the process to reduce energy consumption due to mild reaction conditions. Besides that, they can also work on a wide range of substrates (Taher & Al-Zuhair, 2017).

Ethanol

Ethanol (C_2H_5OH) is the most abundant biofuel in the world and is considered an alternative substitute for gasoline. This biofuel is a key precursor and excellent organic solvent for synthesizing numerous valuable chemical products and other compounds (Ashokkumar et al., 2022). It is also the biofuel with the highest global production capacity and the most advanced in terms of government policies for mixing biofuels with gasoline (Niphadkar et al., 2018).

Ethanol production has gone through many technological advancements that have increased global production capacity (Gavahian et al., 2018). Most commercial ethanol production plants rely on sugar and starch-based raw materials, such as corn in the US (Mohanty & Swain, 2019), sugar cane in Brazil (Paulino et al., 2018), and wheat, sugar beet, and barley in Europe (Friedl, 2019; Marzo et al., 2019).

Although the production of 2G ethanol is still in its early stages, some well-known industries such as DuPont, GranBio, Poet-DSM, Raízen, and Abengoa have already invested to launch commercial plants soon. Bioethanol synthesis can be achieved through thermochemical and biological routes. In both methods, the recalcitrant lignin portion is degraded into simple fragmented molecules of intermediate products and then converted into composite ethanol (Ashokkumar et al., 2022). Enzymatic hydrolysis can also be used to produce bioethanol through syngas fermentation (using *Clostridium* sp.). The cellulase and hemicellulase enzymes can help hydrolyze the corresponding lignocellulosic components into monosaccharides (sugar) followed by a fermentation reaction with yeast and bacterial species to produce ethanol (Ashokkumar et al., 2022).

Biogas

Biogas is an important source of renewable energy that can replace gasoline for producing heat and energy. It is made up of gases produced by organic matter undergoing anaerobic digestion (without oxygen) or bio-methanation, mostly consisting of carbon dioxide (CO_2) and methane (CH_4) and trace amounts of hydrogen sulfides and siloxanes. The digestion process is carried out by anaerobic organisms which can break down biodegradable materials such as green waste or food waste, agricultural waste, plant materials, municipal waste, sewage, and compost in a closed system (Ashokkumar et al., 2022).

The closed system of the fermentation process is referred to as a bioreactor or biodigester, or anaerobic digester. Producing biogas offers excellent opportunities to develop the economies of rural populations and can provide various job opportunities through the adaptation of waste management and biomass valorization technologies. The efficiency of biogas production techniques is mainly influenced by different factors such as pH, temperature, mixing, retention time, C/N ratio (carbon to nitrogen), and organic loading rate (OLR) (Ashokkumar et al., 2022).

However, the usefulness of lignocellulosic-based raw material in the anaerobic digestion process is limited due to the recalcitrant nature of the biomass' internal

components leading to low digestion and biodegradation performance (Ashokkumar et al., 2022). Other developments are focused on incorporating various co-digestion processes, implementing different pretreatment methods, microbial inoculation, and applying chemical additives (NaOH and CaO) and biological additives (white and brown rot fungi) to enhance microbial growth and biogas production rate (Mao et al., 2015).

Biojet (biokerosene)

Biojet fuel is usually prepared through biochemical and thermochemical routes by converting various biogenic wastes and hydrotreated vegetable oil as the main raw material (Eswaran et al., 2021). Currently, hydrotreated vegetable oil is considered the most promising and scalable route for biojet production (Zelt, 2018). Hydrotreated Vegetable Oil (HVO), also known as "green diesel," is currently popular as a blending component for fossil diesel fuel. The production of HVO involves the catalytic hydrodeshydrogenation of triacylglycerols in vegetable oils, followed by the separation of water and unwanted light components (Mittelbach, 2015).

The synthesis of bio-kerosene from lignocellulose can be achieved through two possible approaches: (i) the raw material is directly converted into sugars through hydrolysis followed by bio-kerosene synthesis, (ii) the raw material is first converted into intermediate products through thermochemical treatment and then upgraded to bio-kerosene (Ashokkumar et al., 2022). Microorganisms consume the sugar in the medium and produce isoprenoids, such as farnesene and pyrene, which will later undergo a hydrogenation process, resulting in bio-kerosene. Alternatively, the raw material can undergo pyrolysis, gasification, or liquefaction thermochemical treatment to produce the intermediate products, which are later upgraded to bio-kerosene (Buchspies & Kaltschmitt, 2018).

The high price of biojet makes it even harder for the product to be developed for commercial use on a large scale compared to conventional fossil fuels (Zelt, 2018). These issues can be overcome by establishing efficient intergovernmental policies to reduce taxes associated with supplying biofuels and developing alternative routes in biojet production methods, along with valuable co-products that can generate practical accessibility (Ashokkumar et al., 2022).

Challenges and Future Perspectives

Many countries are behind in implementing specific long-term plans and policies to efficiently collect and recycle waste. Most commercially available plants for chemical and biofuel production are not economically feasible due to pre- and post-processing technologies (Okolie et al., 2021). Future work needs to focus on methods for different biomass collection strategies to ensure a continuous supply of raw material, and on developing cost-effective approaches for biomass conversion with considerations for developing new, cheap, environmentally friendly, and efficient catalysts, catalyst supports, and hybrid catalytic structures (Tran et al., 2019). A wide range of homogeneous and heterogeneous catalysts is used in most cases to improve the efficiency of the process. However, its use has challenges such as high cost, catalyst recovery, and regeneration and toxicity problems (Karmee, 2018).

To overcome these limitations, the promising development of the process coupled with economic

evaluation, including operational cost analysis, will guide the potential way to design a successful biorefinery. A technical-economic evaluation is crucial for sustainable lignocellulosic valorization and is an important analysis tool for biorefinery schemes as it provides decision-making data for the investment process (Ashokkumar et al., 2022).

The integrated biorefinery in the bio-circular economy is a concept of a process that involves the valorization of lignocellulosic biomass into high-value-added products, including biofuels, bio-based chemicals, and biomaterials (Baskar et al., 2020). A biorefinery is a specific integrated process project capable of producing various bio-based products. However, not all biorefinery technologies can be implemented on an industrial and commercial scale due to limitations such as technological innovation, funding, and market demand (Mussatto & Bikaki, 2016).

The development of the integrated biorefinery concept is gaining attraction and relies on lignocellulosic biomass for many bio-based products. However, designing a generic process for lignocellulosic materials is challenging due to unique characterization measurements and its multivariant and multi-scale recalcitrance phenomenon. A deeper understanding of the scope of pretreatment development and leveraging the advancement of omics technologies, high-yield approaches, or CRISPR/Cas9 systems may overcome the obstacles in processing materials and enhance the generation of bioproducts from various lignocellulosic substrates. It is also essential to predict the challenges and potential reliability behavior of the designed technologies or strains in commercial operations (Ashokkumar et al., 2022).

Thus, efficient conversion processes could be developed that focus on producing various substances rather than generating a single product. The concept of integrating one or more biomass conversion technologies to produce a wide variety of bio-chemicals and biofuels should also be investigated as part of future research (Okolie et al., 2021).

FINAL THOUGHTS

Although lignocellulosic biomass is a renewable, low-cost, and promising raw material for sustainable energy production, there are still technological barriers to its economically viable and large-scale production. This review showed that there is an increasing need for research and investment in the adoption of lignocellulosic biomass in the production of second-generation biofuels.

Efficient techniques for converting cellulose, hemicellulose, and lignin into bioenergy are still needed. The goal is to improve the digestibility of these materials and to develop cost-effective conversion technologies. Additionally, improving the efficiency of different steps in the process through advances in pretreatment methods and enzymes that improve hydrolysis, as well as developing more tolerant and capable fermenting microorganisms, are key points to be developed. So far, metabolic and microbial engineering has made significant progress in improving the yield of biofuel production from biomass materials.

Finally, this narrative review has embraced the concept of turning waste and environmental liabilities into wealth and environmental-economic assets by exploiting the abundance of underutilized lignocellulosic biomass to produce biofuel, towards a sustainable circular economy and an environmentally correct future.

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