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Harnessing rice husks: Bioethanol production for sustainable future

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ABSTRACT

The investigation of biofuel production from rice husks highlights its potential as a sustainable energy source amid rising environmental concerns and the gradual loss of fossil fuel sources. Biomass-derived biofuels, notably those derived from lignocellulosic materials, such as rice husks, provide a sustainable and environmentally friendly alternative that reduces greenhouse gas emissions while improving energy security. This review explores the need to produce biofuels along with the progression of biofuel technology throughout the four generations and the specific mechanisms involved in the conversion of bioethanol from rice husks. Several important stages are essential for the production of bioethanol from rice husks, including the disruption of lignocellulosic structure known as pretreatment, hydrolysis of complex carbohydrate structures into fermentable sugars, fermentation utilizing suitable microorganisms to produce ethanol, and purification of the end product by distillation. Despite significant advances, these systems still encounter challenges in terms of their costeffectiveness and efficiency. Pretreatment techniques generally require considerable amounts of energy; the quantity of lignin influences hydrolysis effectiveness, and the process of fermentation must be carefully adapted for higher yields. This study emphasizes the need for continuing research and advancements to eliminate these obstacles. Improvements in pretreatment technologies, enzymatic applications, and fermentation procedures are essential to enhance the efficiency and cost-effectiveness of rice husk bioethanol production. By emphasizing these areas, rice husks' potential utilization as a valuable biofuel source could assist in achieving long-term energy goals while lowering the negative environmental impact of energy generation.

Introduction

Natural resource shortage has become a significant problem in several regions around the world. Worldwide resource scarcity has resulted from rapid population growth and rising industrialization, as well as from emissions of greenhouse gases causing climate change and global warming. The impact of the global climate crisis is a series of progressive repercussions that influence people, animals, and a variety of plants by altering the fundamentals of life, including food security, the destruction along dispersion of habitats. Numerous clean air policies encourage renewable energy resources and demonstrate great efficiency in significantly minimizing the adverse impacts of climate change. Fossil fuels are among the limited resources that are rapidly depleting (Wang and Azam, 2024). "Fossil fuels" refers to nonrenewable carbon-derived sources of energy for instance natural gas, Petroleum, and solid fuels

which are composed of remnants of animals and plants that existed several million years ago and have undergone physical as well as chemical transformation in the lithosphere (earth's crust) (Itskos et al., 2016). Fossil fuels constitute an estimated 80.3 % of the primary energy consumption worldwide, with the transportation sector contributing 57.7 %. Petroleum and other fossil fuels are harmful to the atmosphere and are significant contributors to global changes in climate. CO₂ emissions from fossil fuels are a major source of concern for global climate change. CO₂ emissions in 1990 totalled 22.7 billion tons, rising in 2019 to an estimated 36.44 billion tons, representing an almost 60 % increase. Throughout the years 1990 to 2019, the amount of carbon dioxide emitted from fossil fuels (which include natural gas, coal, and petroleum) grew by 57.5 %, reaching 34.33 billion tons from 21.8 billion tons (Statistical Review of World Energy 2022- all data 1965–2021, 2022). Along with carbon dioxide, the combustion of fossil

Abbreviations: ABE, fermentation- Acetone–Butanol-Ethanol fermentation; ESI, Emergy Sustainability Index; GHG, Green House Gases; RH, Rice Husk; SHF, Separate Hydrolysis Fermentation; SSF, Simultaneous Saccharification and Fermentation; ZEV, Zero-Emission Vehicles.

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fuels emits several other major greenhouse gases (GHGs) including sulfur oxides, carbon monoxide (CO), nitrogen oxide (NOx), particulate matter, arsenic, mercury, volatile organic composites, and heavy metals. The exhaustion of nonrenewable sources of fuel, combined with emissions of greenhouse gas, has developed into an urgent concern (Fawzy, 2020). The concerns brought to light recently regarding the changing climate caused by emissions of greenhouse gases and the crisis concerning energy consumption have highlighted the significance of transitioning from unsustainable energies derived from fossil fuels to renewable, sustainable energy sources (Satari, 2019). In addition, solid waste treatment, which leads to ecological damage, is among the most significant hurdles nowadays, given that we must strive for appropriate means for its handling and eventual disposal in such a manner that it does not impact the environment (Cacua, 2018). As a result, investigating alternatives to tackle the global scale approaching crisis regarding energy, taking into account environmental challenges as well as mitigations at the same time as confronting growing total energy demand, has turned into an essential emphasis (Osman et al., 2021). Several renewable energy sources are gradually emerging as feasible alternatives to fossil fuels, which consist of solar, wind, biomass, geothermal, and hydroelectric energy. Developments in technologies that produce renewable energy have increased as their future potential is better recognized. As a result, understanding the potential global energy landscape is crucial for assessing the role of biomass and other renewable energy sources in pursuing a greener, more sustainable future. Biomass energy offers a significant potential in generating renewable energy while lowering GHG emissions as it is produced by converting biomass into electricity, heat, or liquid fuels. Biomass is critical for combating climate change since it may be rendered carbon-neutral through environmentally friendly methods of land management (Ali et al., 2024). Its advantages over other forms of renewable energy include a constant energy supply, the ability to utilize organic waste, as well as ease of incorporation into existing infrastructure to obtain an effortless switch to renewable energy (Adeleke et al., 2021; Hajinajaf, 2021).

The transportation sector is essential to national and international decarbonization initiatives, accounting for roughly one-fourth of global emissions of greenhouse gases (GHG), most of which are associated with road transport. Furthermore, the transportation sector has emerged as the leading cause of the rise in emissions of GHG in many nations in recent years, accounting for a larger portion of the increase than other sectors (Franzò and Nasca, 2021). Electric vehicles are zero-emission vehicles that are being analysed as a promising solution with potential to decrease the effect on the environment due to the transportation sector. The cost, range, and permanent utilization of battery and fuel cell components, as well as the availability of resources for further production globally, are the main barriers to the current market expansion of zero-emission vehicles, or ZEVs. To ensure the long-term viability of ZEVs, their costs must be reduced through developments, subsidies, and other financial benefits to consumers (Sandaka and Kumar, 2023). In the meantime, the first step toward lowering GHG levels and temperatures can be taken globally with the immediate application of biofuels which are carbon-neutral in current vehicles. Given that consumers can utilize the current existing set-ups and vehicles, the usage of biofuel is heavily endorsed. Additionally, biofuels are generated in substantial quantities and account for at best 2-10 % of the blending, representing a substantial decrease in depency on oil. Over the long term, this approach would reduce GHG emissions while also giving ZEVs enough time to overcome their limits and grow market entrance. ZEV is the unavoidable means of transportation in the future however, biofuels certainly provide the primary encouragement for the change in the transportation industry and decarbonization of the environment (Franzò and Nasca, 2021). Renewable sources of energy must be discovered to meet the constantly expanding demand and declining reserves of energy during this period of energy scarcity and escalating costs of fossil fuels. In order to deduce the world's dependency on non-renewable sources,

alternative options to fuels derived from petroleum, such as bioethanol, are being investigated (Madu and Agboola, 2018).

To support the initiative taken towards biofuel production many countries including India, have incorporated 'Biofuel policies' which refer to plans, aims, and programs for producing and using biofuels such as ethanol and biodiesel. The National Policy for Biofuel 2018 of India is aiming to take forward the suggested target of reaching 20 % mixing of biofuels and fossil fuels by 2030, as well as promoting biofuel nationwide production, in accordance to the Make in India program, by locating units in Special Economic Zones (SEZ) also known as Export Oriented Units (EoUs) (*Press Information Bureau-Government of India*, 2018).

Advantages of biofuels over petroleum

- Biofuels from diverse sources like agricultural and forestry residues
 offer production flexibility as these are manufactured from various
 biomass sources that include agricultural residues, forest residues,
 algae, as well as utilizing dedicated energy crops.
- Biodegradable biofuels are eco-friendly and less toxic than petroleum-based fuel along with addressing long-term energy needs sustainably.
- Biofuel combustion maintains CO₂ balance, unlike fossil fuels, which
 release stored carbon, contributing to greenhouse gas accumulation
 resulting in the emission of fewer pollutants and greenhouse gases
 than petroleum fuels, improving air quality and reducing health risks
 (Gaurav et al., 2017).

Recycling of biofuels from biomass: a value-added approach

Biomass is a non-fossilized organic biodegradable matter derived from animals, plants as well as microorganisms. It encompasses byproducts, debris, and discards from forestry, agriculture along with various other industries, in addition to organic biodegradable and nonfossilized components of industrial and even waste from municipalities (Clarifications of Definition of Biomass and Consideration of Changes in Carbon Pools Due to a CDM Project Activity, 2023). Biofuels are created utilizing biomass/ organic matter, which includes wood, vegetables, seaweeds, and animals. Consequently, biofuel is defined as any hydrocarbon fuel created in a relatively brief amount of time from organic matter that is currently living or originally living. Biofuel is viewed as an energy source security, serving as an alternative to limited-supply fossil fuels, along with being an environmentally beneficial fuel as biomass is classified as carbon-neutral or atmospheric greenhouse gas negative (GHG neutral) (Itskos et al., 2016). Biofuel manufacturing is a feasible energy source and a resolution for these challenges, given that it offers a sustainable and renewable energy source derived from plants, agriculture, non-edible food waste, home wastes, etc., which are utilized in day-to-day life (Saha, 2018). Biofuels are sustainable and derived from agricultural produce, including sugarcane, oleaginous vegetation, forest biomass, and other organic materials which are utilized either alone or as an addition to a mixture with other traditional fuels (Osman et al., 2021). Examples include biodiesel, ethanol, methanol, methane, and charcoal. During the last few decades, the production of manufacturing mechanisms of fuels derived from biomass has progressed from first to fourth-generation biofuels, which traverses subsequent generations. The 1st, 2nd, 3rd, and 4th generations of biofuel consist of agricultural produce, indigestible biomass, macroalgal or microalgal biomasses, genetically altered algae, and ecosystems of microbes (Osman et al., 2021).

Biofuel is characterized as 1st, 2nd, 3rd, and 4th generation biofuel on the basis of their biomass source benefits, drawbacks, along with technological advancement. The most prevalent forms of biofuel are 1st and 2nd-generation biofuel, although 3rd, and 4th-generation biofuels have acquired popularity since 2010 and these are currently in development phase (Ale et al., 2019). 1st-generation biofuel is obtained from food, and hence competition with food may pose a significant challenge

to their use. Crop residue, forest, waste from animals, and wood can be utilized to extract biofuels from a 2nd generation i.e., biodiesel, bio-hydrogen, bioethanol, and bio-butanol with the byproducts being redeveloped into fertilizer. Furthermore, algal-based biofuels with better efficiency per unit area than conventional biofuel are considered 3rd-generation biofuels, whereas genetically engineered microorganisms make up 4th-generation biofuels, which remain under investigation (Kumar, 2020). Ale et al. (2019) suggested that the 1st as well as 2nd generations of biofuel are primarily utilized, while the remaining generations are currently underdeveloped and investigated (Table 1).

1st generation biofuel

1st -generation biofuel mostly originates from consumable food sources including vegetable oil, sugar, and starch. They are sometimes referred to as traditional biofuels that include ethanol produced through the fermentation of sugar beets or sugarcanes. 1st -generation biofuels comprise biogas, bio-alcohols, and biodiesel (Saha, 2018). While rape-seed (Brassica napus) and soybeans [Glycine max (L.) Merr.] is utilized to make biodiesel, wheat, maize, and sugar cane (Saccharum officinarum) are a part of the most often employed feedstock for the production of bioethanol. China's primary components for bioethanol production are wheat and maize, whereas India produces ethanol from sugar cane along with various oil crops (Ale et al., 2019).

Table 1Advantages and disadvantages of Four generations of biofuels.

Generations of Biofuels	Feedstock used	Disadvantages	Advantages	References
First generation	• Corn • Sugarcane • Soyabean • Rapeseed	1. Competes with food supply as a result impacting food prices and availability 2. Limited sustainability of biofuel produced	1. Utilizes existing agricultural products 2. Relatively simple processes	(Thallada and Pandey, 2015)
Second generation	Corn stover Wheat/ Rice straw/ husk Wood Organic waste	Requires costly and advanced technologies The pretreatment step of lignocellulosic biomass can be energy-intensive	Reduces competition with food crops Utilizes agricultural and forest residues improving overall sustainability	(Hajilary, 2018)
Third generation	Algae	Requires significant research and development High initial capital costs Harvesting and processing of algae is a bit challenging	High yield potential from algae Avoids competition with food crops Easily grown in marginal lands	(Ale et al., 2019)
Fourth generation	Genetically engineered crops	Still largely in the research and development phase High costs associated with genetic engineering and synthetic biology Regulatory and ethical concerns	Potential for highly efficient production Utilizes advanced biotechnology Can achieve a negative carbon footprint	(Pattnaik, 2024)

2nd generation biofuel

2nd generation biofuels, commonly known as "olive greens" or "cellulosic ethanol" fuel, are mostly derived from sustainable or non-food feedstocks/ biomass. Edible waste oils, forest residues, industrial residues, and sustainable biomass are the principal feedstocks used to produce second-generation biofuels (Saha, 2018). Wood, bagasse from sugarcane, organic debris, stover from corn, wheat, or rice straw, as well as rapidly-growing plants like poplar, are some of the feedstocks used to produce second-generation biofuels (Ale et al., 2019). The majority of the constraints accompanying the development of 1st -generation biofuels are solved by 2nd generation biofuels, comprising mostly derived from the lignocellulosic biomasses formed by non-food energy-producing plants and agro-waste.

3rd generation biofuel

3rd generation biofuel is often known as "algae fuel" as they are originated from algae. Algae produce various varieties of biofuels including biodiesel, propanol, butanol, ethanol, and gasoline, with an elevated output nearly 10 times that of 2nd generation biofuel. The production biomass of 3rd generation biofuel also aids in preserving balance of the environment by using atmospheric carbon dioxide(CO_2) (Saha, 2018). Although 3rd generation biofuels are a cost-effective source of alternative energy, producing algal biomass remains difficult in areas for instance Canada, where temperatures are below 0 °C for the majority of the year. Additionally, more studies are required to enhance extraction methods for ethanol including, dehydration technology, to reduce costs related to production and bring 3rd generation biofuel manufacture up to industrial levels. (Thallada and Pandey, 2015; Ale et al., 2019).

4th generation biofuel

4th generation biofuel is the outcome of advances in genetics and plant biotechnology in particular in the carbon capture and storage metabolism bio-engineering process which necessitates the implementation of innovative biofuel-producing technologies. Within this generation, bio-engineered plants or algae serve as carbon capture apparatuses, capturing carbon in various sections, for instance, branches and leaves, to provide biofuel feedstocks (Saha, 2018). This is an evolving field where thorough investigation is currently being performed to identify novel opportunities for the long-term transformation of renewable energy into electricity (Ale et al., 2019). 4th generation biofuels are produced through modified plants and microbes. Each case's feed quality and operation settings vary, consequently, the technologies and final products vary (Thallada and Pandey, 2015).

Second generation biofuels an ultimate approach for sustainable environment

Although both the third and fourth generations of biofuels represent potentially sustainable sources for biofuel production, these are still in development, therefore further investigation is required prior to commercialization of these fuels. The 1st generation of biofuel is derived from ingredients that are edible, raising the food and fodder versus fuel debate, which centers on the effect of biofuel manufacture on food security along with concerns about diverting crops from food to industrial use. Furthermore, first-generation production processes focused solely on manufacturing fuel, discarding all non-fuel elements as waste materials. However, 2nd generation biofuels are composed of inedible materials including agro-waste and forest wastes, and harvests developed specifically for biofuel production (Hajilary, 2018). 2nd generation biofuel techniques constitute an improvement of bioprocesses, lowering total costs related to energy as well as minimizing waste along with the decrease in the reliance on traditional (fossil) fuels. These processes

regarding biofuel production aim to improve fuel retrieval, boost consequent manufacturing of secondary raw components, and generate more beneficial fuels than 1st generation technologies (Hajilary, 2018). These benefits are also essential components of a circular economy because their implementation involves the efficient utilization of waste products and the manufacture of biobased products with no significant adverse environmental impact. The second-generation biorefinery is gaining attention as a consequence of environmental concerns, increasing demand for energy, along global warming, which has prompted interest in bioethanol production as a commercial as well as sustainable biofuel (Pattnaik, 2024).

The biofuels of the second generation are manufactured using lignocellulosic sources. This generation process separates the components of plants lignin and cellulose, which can then be converted into ethanol. These varieties of biofuels can be manufactured utilizing a range of biomass resources, provided that they contain organic carbon. This can be quickly regenerated throughout the process of the carbon cycle (Dahman et al., 2019). The lignocellulose based 2nd generation biorefineries aimed to develop an environmentally friendly in addition distinct economy based on biomass through the utilization of lignocellulosic feedstocks, current conversion technology, and a comprehensive circular economy approach (Pattnaik, 2024). There are numerous sources of plant lignocellulose, including rice, which is one of the most common agricultural wastes in India, generating a vast volume of debris known as rice husks. Rice husk/hull is a significant secondary derivative of the industry processing rice and belongs to the most widely accessible lignocellulose-based biomass sources which can be adapted into solid pellets and utilized as an effective substitute for conventional fuels such as diesel and coal (Defonseka, 2018).

Harnessing biofuels from lignocellulosic waste

Bioethanol is created from prevalent and sustainable non-food resources to replace traditional biofuels, often known as first-generation biofuels. Currently, commercialized bioethanol is manufactured from the starch of maize and sucrose from sugarcane grains, which fight for cultivable area and food production. Apart from the fact that these crops cultivated for food have been processed to boost production in extremely short time periods, the potential use of these sources of food for the manufacture of ethanol could only worsen the current energy and food crises as the human population increases. Lignocellulose-based biomass is viewed as a promising feedstock as a potential ethanol source because of its widespread accessibility, lower costs, along with a lack of conflict with conventional sources of food while providing a viable substitute for fossil fuels, the widespread usage of which depletes global stocks, in addition, leads to environmental destruction (Sjulander and Kikas, 2022). The introduction of biofuels as a fossil fuel substitute is a step toward diversification of energy, which is the addition of several energy supplies to the mix of energy sources used in energy generation i. e., elevating the energy produced proportion of every source in order to prevent a country's entire reliance on a singular source of energy. To achieve sustainable economic development and reduce the adverse effects of climate change, diversification of energy through increased investments in energy sources which are renewable is anticipated to decrease emissions of greenhouse gases from fossil fuels (Akrofi, 2021).

Lignocellulose biomass is envisioned as a plentiful carbon-neutral renewable supply capable of lowering $\rm CO_2$ emissions and air pollution. Thus, it is a possible alternative for reducing crude oil, as it can potentially be utilized to make biofuels, biomolecules, and biomaterials (Isikgor and Becer, 2015). Furthermore, cellulose, the main constituent of lignocellulose-based biomass, is regarded as the most promising choice for replacing petroleum-based fuels given its ecologically beneficial properties such as biocompatibility, biodegradability, and renewability (Mäki-Arvela et al., 2010; Isikgor and Becer, 2015). Lignocellulosic wastes are commonly derived from industrial debris (paper manufacturing discard, sawdust, and food processing waste),

forestry waste (hardwoods as well as softwood), agricultural waste (such as straw, husks/hulls, strove, and non-food items like seeds), household residues (e.g., kitchen waste products, sewage, as well as waste paper), and solid waste from municipalities (Behera et al., 2014; Satari, 2019). Lignocellulosic plant materials are affordable and readily available. However, depending on the constitution and form of a given plant, its individual elements may be challenging to ferment or break down biologically (Anamika et al., 2022).

Lignocellulosic residues formed during rice processing, such as husks and chaff, which are left at the collection site, are rendered low-value resources and, in some circumstances, waste. Rice husks contain a high concentration of polysaccharides, including hemicellulose and cellulose, making them a potential resource for the manufacture of fermentable sugars (Cacua, 2018). Rice husks have been traditionally managed by directly dumping them into the ground and then composting them or burning them for fuel. This burning emits a large number of small particles into the atmosphere; however, composting has been found to be inefficient owing to its inadequate nitrogen concentration. In some countries, rice husk ash, or RHA, ends up being disposed of in land used for farming, where the silica concentration not only decreases soil fertility but also poses a hazard to the environment as well as human well-being (Baniya et al., 2020). As a result, it is especially important to appropriately dispose of rice husk biomass, highlighting it as an appealing alternative for bioethanol manufacturing because it serves two goals in one solution (Tripathi, 2016; Cheng and Wang, 2017). Rice husks are also utilized as feedstock for several chemical processes such as gasification and pyrolysis, which generate bio-oil as an alternative to diesel. Other biomass sources can be utilized in addition to rice husks, if required for specific qualities or economic reasons (Defonseka, 2018).

The maximum reported bioethanol yield for sugarcane bagasse was 38.02 L/t of bagasse by biomass which is alkaline pretreated (Carvalho et al., 2016), while for rice husk with alkali pretreatment, it was found to be 250 L/t of dry feed and for sorghum bagasse, it was found to be 134 L/t of dry feed (Barcelos et al., 2016). The information in Table 2 indicates that the yield of bioethanol from rice husk is comparatively higher than other lignocellulosic biomasses treated with Alkali pretreatments (Jain and Kumar, 2024).

Emergy is known as the amount of one type of energy that gets utilized either directly or indirectly during the process of transformation of a product or service. Indices based on emergy present information about the thermodynamic efficacy of manufacturing, the quality of manufacture, and the relationships involving the process and its surroundings. The ESI is Emergy Sustainability Index which is a multidimensional indicator of long-term sustainability. The higher the value of the ESI, the greater the financial and environmental synchrony of the manufacturing procedure in terms of substitutes producing the same products (Liu et al., 2016; Mandade et al, 2016).

Mandade et al. (2016) discovered that the average emergy sustainability index (ESI) of rice husk was 0.62, the higher among the various lignocellulose feedstock evaluated. Amongst all the lignocellulose-based feedstocks taken into consideration in this investigation, comprising sorghum stalk, wheat stalk, cotton stalk, and bagasse of sugarcane, the ethanol from rice husk demonstrated the highest renewability because of the involvement of rainwater subsisting more extensive compared to remaining feedstocks. Although there isn't any ideal raw material, rice husk, as well as cotton stalk, were the most promising of the biomasses examined in this study. Rice husk to ethanol manufacturing has a smaller negative environmental effect than other feedstocks since it uses fewer non-renewable materials in the process of production cycle and hence it was established that the production of ethanol utilizing rice husk biomass was the best of the feedstocks studied.

Rice husk: waste to energy

Rice constitutes one of the largest and most important staple meals

Table 2The maximum reported bioethanol feedstocks utilizing Alkali pretreatment.

Raw material	Pre-treatment processes	Down-stream processes	Yield (L/t of dry feed)	Temp. (°C)	pН	Fermentation time (hours)	References
Sugar cane Bagasse	Alkaline extraction	SSSF	38.02	37	4.8	22	(Carvalho et al., 2016)
Rice Husk	Alkali pretreatment (5 % NaOH)	SHF	250	30	5.5	-	(Jain and Kumar, 2024)
Sorghum Bagasse	Alkali Pretreatment	SSF	134	37	4.4	60	(Barcelos et al., 2016)

for humans, accounting for 50-80 % of daily caloric intake. One of the top producers of brown and white rice worldwide is India. From 2014 to 2016, rice production in India climbed from an average of 160.2 million tons to an unprecedented record high of nearly 166.5 million tons (111.0 million tonnes milled) (Food and Agriculture Organization (FAO), 2018). The matured grain of rice is cultivated in the form of coated grain (rough grain or paddy), containing caryopsis i.e., brown rice protected by a strong siliceous husk. Rice hulls, commonly known as husks /chaff, constitute the outermost convex hard layers/shells that protect rice granules (Juliano and Tuaño, 2018). A rice kernel is composed of two layers: an inner layer termed bran and an outer layer called husk, which is commonly thrown away or burned as waste (Singh, 2018). Rice husks (RH) are a major agricultural waste produced in rice-growing countries (Prabhakaran et al., 2017). Every year, roughly 120 million tonnes of rice husks are available after being extracted from the entire rice paddy (Lim et al., 2012).

Currently, only around 20 % of the straw produced from rice is utilized for feasible applications including biofuels, papers, fertilizers, as well as animal feeds. Following the harvest, the majority is burned agricultural land, mixed into the soil, otherwise employed as mulching for next season's crops. However, the straw placed in the soil disintegrates gradually and could possibly carry diseases whilst burning has grown increasingly objectionable due to considerable pollution of the atmosphere, involving emissions of greenhouse gases and soot. The annual global production of rice in 2022 was recorded as 776.4 million tons and as around 20 % of the rice paddy is husk, 155 million tons of rice husk waste was generated in 2022 alone (FAOSTAT, 2022). Rice husks are a widely available recyclable material across every rice-manufacturing country and consist of approximately organic carbon (30–50 %). Approximately 20 % of rice is made up of rice husks,

which are mostly composed of approximate amounts of cellulose, lignin, silica, and moisture which are 50 %, 25–30 %, 15–20 %, and 10–15 %, respectively (Singh, 2018). For each kg of milled white rice, 0.28 kg of rice husk is estimated as a by-product of the manufacturing of rice in the process of milling is generated. In 2017, 769.75 million tons of straw from rice in addition to 153.95 million tonnes of rice husk had been manufactured worldwide, which could have generated 638.03 PJ worth of energy (Mofijur et al., 2019); these various sources of energy generation using rice husk are stated in Fig. 1.

Rice husks are commonly used to make solid fuel i.e., loose forms such as briquettes, and pellets, carbonized rice husks which are made after combustion, and residual rice husk ash. Despite their diverse applications, their financial advantages and contributions have not received adequate attention (Bodie et al., 2019). Gasification is an alternate procedure that converts rice husk into syngas in a reaction chamber with a specified amount of air. Syngas can be employed as a fuel for either cooking, drying, or power generation. In rural regions, rice husk are utilized as feeds for cooking in rice husk stoves (Baniya et al., 2020). However, it has recently received attention for its possible use in the manufacturing of biofuels from rice husk pellets as a sustainable energy source to provide a viable substitute for petroleum-based fuels (Defonseka, 2018). A significant source of lignocellulose rice husks is considered and may serve as a feasible feedstock for bioethanol manufacturing if pre-treatment techniques are properly chosen, effective saccharification enzymes are used, and fermentation conditions are adequate.

Types of biofuels recycled from biomass

The production of biofuels, particularly ethanol and biodiesel,

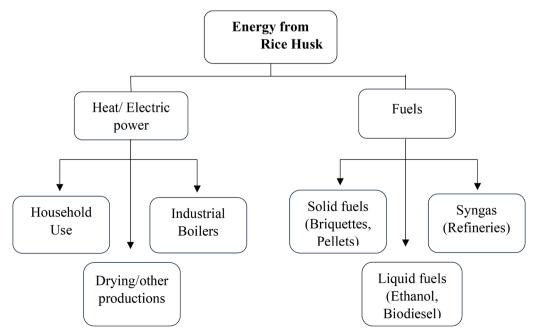


Fig. 1. Energy production from Rice Husk (Rice husk; Mofijur et al., 2019).

reached 159 billion L worldwide in 2019. Of the 115 billion litters of 1 G ethanol manufactured worldwide, the United States comprised 48.2 % whereas Brazil produced 26.7 % generating around 75 %, while production of half of the world's biodiesel (41 billion litters) was achieved by the European Union manufacturing 32.3 % and 18.1 % by the United States (OECD-FAO Agricultural Outlook 2022–2031, 2022).

Biodiesel

In the transportation industry, biodiesel serves as a biodegradable and sustainable liquid fuel that replaces diesel made from petroleum (Uthandi, 2022). Biodiesel is produced via the esterification of vegetable oil, alcohol (methanol or ethanol), and animal fat with the use of an acidic or basic enzyme catalyst. Transesterification is also used to produce biodiesel. Even though it is thought to have a slightly inferior fuel effectiveness than standard diesel, it is nevertheless a clean combustibility with no sulfur or aromatics, increased lubricating properties, and biodegradable properties. Renewable energy sources have great green credibility due to these biofuels' attributes. Based on where they are produced, biodiesels are separated into three generations (Gupta and Gaur, 2019). Biodiesels are classified into three generations according to their source of manufacturing. Based on where they are produced, biodiesels are separated into three generations. Edible feedstocks like corn, rapeseed, mustard, coconut, rice, and soybean oil are commonly used to create biodiesel for the first generation. Whereas, 2nd generation is made using oils that are non-edible like those found in neem, rubber seed, milk bush, petroleum nuts, Mahua indica, Jatropha, and Karanja. Higher oil content sources can be used to create second-generation biodiesel. Finally, 3rd generation biodiesel is produced using waste oils and microalgae. These days, 1st generation biodiesel is produced in enormous quantities and combined with diesel derived from fossil fuels (Ambat et al., 2018; Singh, 2023). Biodiesel manufacturing employing oil extracted from rice bran or rice husks minimizes the total expenses whilst producing a high yield in shorter reaction times with operating temperatures of 60 °C to 70 °C. The use of a varied catalyst constructed from rice husks provides a supplementary advantage. The implementation of rice husk as a catalyst source was equivalent to that of an alkyl catalyst, presenting it as an effective and affordable source that can improve the procedure's sustainability (Gaur, 2021).

Bioethanol

Bioethanol is a sustainable biofuel that is manufactured through the ABE(Acetone-Butanol- Ethanol) fermentation of various feedstocks including wheat straw, maize, soybeans, woodchips, microalgae, and

Table 3Bioethanol production sources.

Generation of biofuel	Type of feedstock	Source	References
First generation	Sugar-based	Sugarcane,MolassesSugar beetSweetsorghumRapeseed	(Thallada and
bioethanol	feedstock		Pandey, 2015)
	Starch-based feedstock	Wheat grains Corn Barley grains Soyabean Maize	(Saha, 2018)
Second generation	Lignocellulosic-based	Rice straw/	(Ale et al., 2019)
bioethanol	feedstock	husk Wheat straw Corn straw Bagasse	

many other sources as shown in Table 3. It contains 35 % oxygen and is capable of reducing automotive emissions. This biofuel can be utilized directly in vehicles and operates similarly to conventional fuels. Additionally, due to its high-octane rating, bioethanol allows for increased engine compression ratios, which enhances engine performance and efficiency (Ethanol fuel Basics- US Department of Energy, 2015). In comparison to gasoline, which lacks oxygen, bioethanol is an environmentally beneficial oxygenized fuel, containing 34.7 % oxygen. This results in approximately 15 % greater combustion effectiveness for bioethanol than gasoline, leading to lower emissions of particulate matter and nitrogen oxide (Zabed et al., 2017; Dahman et al., 2019). Rice husk, a substantial byproduct from the rice processing industries, represents a particular one of several feedstocks made up of lignocellulosic material. Due to its 68.22 % content of carbohydrates that are cellulose and hemicellulose, the matter is capable of being utilized to produce biofuels through the fermentation process (Germec et al., 2016).

Bioethanol, a clear liquid, is the most extensively produced biofuel worldwide, with the United States and Brazil being the primary producers. In 2016, global manufacturing reached 18.3 million tons. That year, the European Union produced 310,000 tons, accounting for 17.8 % of the EU's total liquid biofuel production. Biodiesel is the most commonly used biofuel in the EU. Despite lower production compared to other regions, the EU has experienced consistent growth over the past decade (Zabed et al., 2017; Golušin, 2023). Currently, the global manufacture of bioethanol using rice, wheat, corn, and bagasse is of particular interest. Out of these four agricultural wastes, rice husk contains the greatest possibility of producing 205 billion liters of bioethanol annually, making it the most plentiful waste when in comparison with the other significant wastes (Sarkar et al., 2012). The current market scenario of bioethanol production worldwide is shown in Fig. 2.

Conversion of lignocellulose to bioethanol

There are two methods for transforming lignocellulosic biomass into biofuels: thermochemical and biological conversion, with biological conversion being the more frequent technique for producing ethanol than thermochemical conversion owing to its excellent efficiency of conversion and selectivity (Wang and Lee, 2021). The transformation of lignocellulosic biomass to produce bioethanol includes a pretreatment phase that follows enzymatic hydrolysis and sugar fermentation (Kapoor et al., 2020). The process begins with the mechanical reduction of size, followed by pretreatment, which further disrupts and separates the biomass structure. This is followed by hydrolysis, which degrades polysaccharides into monomers, such as arabinose, glucose, and xylose. Throughout fermentation, simple carbohydrates such as glucose are transformed into ethanol (Al-Mardeai et al., 2022). Fermentative species qualified for C5 breakdown include yeast (Pichia stipites and Saccharomyces cerevisiae) along with bacteria (Clostridium thermocellum and Zymomonas mobilis) (Wang and Lee, 2021; Mujtaba et al., 2023). The complete process of bioethanol production from lignocellulosic biomass including the disposal of processing byproducts is given in Fig. 3.

Pretreatment

Pretreatment is an important step in biochemical processing that converts lignocellulosic biomass into products such as bioethanol. The chemical composition of cellulosic biomass must be modified to create cellulose readily available for enzymes to convert carbohydrates into sugars which are easily fermentable. The pretreatment step is essential to break the arrangement of lignin along with disrupting the crystallized cellulose form, allowing acid or enzyme to readily dissolve cellulose and hydrolyze it into monomers (Zhang et al., 2011). Pretreatment techniques, either alone or in combination, can improve waste biodigestibility for biofuel production, while also increasing enzyme accessibility. It increases the digestion of problematic biodegradable substances coupled with the output of biogas and ethanol using waste.

2023- Annual ethanol production(Mil. Gal.)

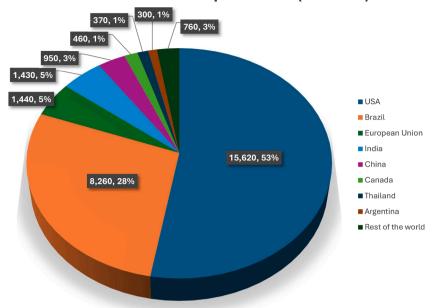


Fig. 2. Annual ethanol production of 2023 (Annual Ethanol Production- U.S. and World Ethanol Production, 2023).

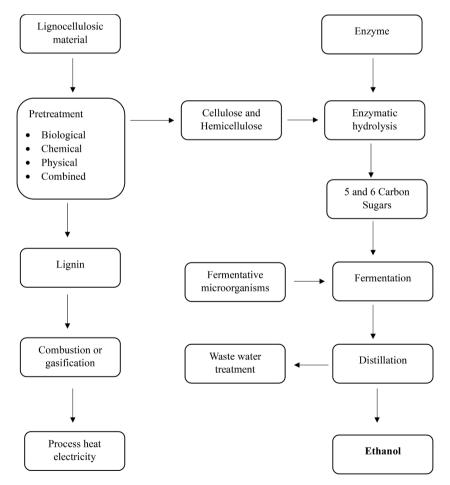


Fig. 3. Process of conversion of Lignocellulosic biomass (Rice husk) to Bioethanol (Kapoor et al., 2020; Al-Mardeai et al., 2022; Mujtaba et al., 2023).

Pretreatment is often the costliest stage of the procedure of transforming biomass into fuel, but it has the potential to improve efficiency and reduce costs through further exploration. Recent studies have found

a link connecting the process of lignin removal and hemicellulose in addition to the cellulose ability to be broken down (Alvira et al., 2010). Physical techniques like chipping, milling, and grinding can increase

crystallinity, and reduce the size of particles while increasing the surface/volume ratio, but they can also be expensive concerning utilization of energy and investment. Chemical pretreatments, that involve the use of chemicals such as alkalis, ozone, peroxide, or organic solvents, are primarily focused on removing lignin and increasing the enzymatic degradability of cellulose. The ideal pretreatment method cannot be determined with regard to various factors, including the type of lignocellulose biomass and the intended products (Lamsal, 2010).

A successful and cost-effective pretreatment should fulfill several requirements, including the production of receptive cellulosic fiber for enzymatic attack, preservation of cellulose and hemicelluloses, prevention of enzyme and microorganism inhibitors, reduction of energy consumption, feedstock size reduction costs, material costs for reactor construction, and generation of fewer residues, all while using inexpensive or no chemicals. Pretreatments should increase lignocellulose biomass digestibility and every pretreatment method has a unique influence on fractions of hemicellulose, lignin, and cellulose. Acid-based pretreatments are favored for industrial ethanol production, where lignin is left in the substrate and removed through (hemi)cellulose hydrolysis or distillation. By removing lignin from the biomass at the beginning of the procedure, it is possible to be retrieved as a high-value co-product such as an alternative energy source to electricity. Additionally, enzymatic hydrolysis is directly associated with lignin content, and removing lignin significantly improves the process of enzymatic hydrolysis (Isikgor and Becer, 2015).

Hydrolysis of pre-treated rice husk

The process of converting the hemicellulose and cellulose components of lignocellulose biomasses into fermentative sugars is known as hydrolysis (Lamsal, 2010). Pretreatment of biomass typically yields two portions: a water-insoluble solid portion consisting mostly of lignin and cellulose, and an aqueous component composed of hemicellulose and corresponding sugar. The degree of hemicellulose hydrolysis can vary depending on the pretreatment procedures and circumstances used, with incomplete depolymerization resulting in the transformation of hemicellulose into oligosaccharides that require additional hydrolysis. On the other hand, cellulose remains largely unconverted during pretreatment and requires a separate hydrolysis process for conversion of glucose (Gírio, 2010; Zabed et al., 2017).

Hydrolysis is necessary to convert carbohydrates like cellulose, hemicellulose, and starch into fermentative sugars, as yeast are unable to use these carbohydrates as substrates. Enzymatic or Acidic processes can be employed to hydrolyze the hemicellulose, cellulose, and starch, and the outcome is influenced by the biomass composition and type, in addition to the conditions of hydrolysis (Liu et al., 2016; Zabed et al., 2017). Concentrated acidic hydrolysis has proven to be a successful hydrolysis technique because of its low process temperatures and lack of the need for enzymes. Nevertheless, the corrosion of instruments with an elevated acid concentration is a substantial disadvantage of the procedure. Enzymes may hydrolyze both hemicellulose and cellulose to manufacture sugars that are soluble at a comparatively lower temperature starting from 45 °C to 50 °C while causing minimal corrosion of the equipment (Zabed et al., 2017).

While cellulose hydrolysis has been conducted with acids or enzymes, enzyme-mediated hydrolysis has proven to be more appropriate because no secondary components from sugars are generated and a lower temperature for the process is required. In summary, hydrolysis aims to release the plant cell wall monosaccharides from polysaccharides, and this hydrolysis of polysaccharides like hemicellulose and cellulose produces fermentative sugars which can be converted into ethanol through the process of fermentation.

Fermentation

The fermentation process aims to effectively convert pentose(C5)

and hexose(C6) sugars into ethanol employing fermentative microorganisms like yeasts. Bacteria regarded as ethanol-producing are vulnerable to lignocellulosic hydrolysate, influenced by the fermentation conditions and bacterial strain. Fermentation processes are classified into two types: separate hydrolysis fermentation also known as SHF and simultaneous saccharification and fermentation also known as SSF. These fermentation techniques are frequently used in the ethanol manufacturing process. The SHF process consists of two steps: saccharification, which is the breakdown of cellulose into fermentative sugar, and fermentation, which converts these sugars into bioethanol. However, ethanol production using the SSF process is capable of simultaneous completion in a singular step, resulting in an elevated yield of ethanol. This approach has also been shown to have lower production expenses than SHF. However, SSF requires suitable fermentation and saccharification conditions, particularly temperature (Madu and Agboola, 2018; Satari, 2019). For a distinct representation of both techniques, Table 4 illustrates the comparison of both techniques in a concise manner.

Yeast (Saccharomyces cerevisiae) has historically been utilized for 2nd generation production of bioethanol due to its capacity for fermentation along with tolerance to ethanol, low nutritional need, and fewer byproducts (Madu and Agboola, 2018; Roukas and Kotzekidou, 2020). However, this bacterium only ferments hexose sugar. Several types of yeasts and bacteria can ferment pentose sugars which are denoted in Table 5. Among different bacterial species, Z. mobilis is primarily employed to produce bioethanol; diverse strains ferment glucose (C₆H₁₂O₆), sucrose (C₁₂H₂₂O₁₁), and fructose (C₆H₁₂O₆), whereas genetically modified strains ferment sugars like arabinose (C5H10O5) and xylose (C₅H₁₀O₅) (Van et al., 2013; Meltem and Benjamin, 2016). Furthermore, Z. mobilis offers better bioethanol output, and efficiency is roughly 2.5X more rapid in comparison to that of S. cerevisiae (Mishra and Ghosh, 2019). In order to obtain maximum results, Li et al., 2022 developed a combined procedure for anaerobic fermentation to transform lignocellulosic biomass into ethanol using the combined cultivation of Z. mobilis ATCC 31,821 with Pecoramyces sp. F1. The benefits of this integrated process consist of low cost as no need to inject O2 as

Table 4Comparison between the two main fermentation techniques.

Fermentation techniques	Advantages	Disadvantage	References
Separate hydrolysis fermentation (SHF)	Allows optimization of each step independently for maximum efficiency Easier to control process conditions and troubleshoot issues Higher potential enzyme activity due to optimal conditions	Requires more equipment and process steps, increasing costs and complexity Higher risk of contamination due to multiple handling stages Longer overall process time compared to SSF	(Madu and Agboola, 2018)
Simultaneous saccharification and fermentation (SSF).	Combination of enzymatic hydrolysis and fermentation into a singular step, reducing process time and costs Decreases the risk of contamination due to fewer stages and lower sugar concentrations Can achieve a higher overall conversion efficiency	1. Optimal conditions for hydrolysis and fermentation may differ, leading to compromises in process parameters 2. Enzyme activity might be inhibited by ethanol produced during fermentation 3. Limited flexibility in adjusting individual process stages	(Satari, 2019)

Table 5

Optimized pretreatment strategies employed for the production of Bioethanol from rice busk

Fermenting Organisms	Chemical pretreatment	Hydrolytic enzymes	Bioethanol Yield/ Saccharification	References
Saccharomyces cerevisiae	0.1 M of FeCl3, HCl, and NaOH	Trichoderma reesei cellulase	$\begin{array}{c} 3.802 \pm 0.041 \\ \% \end{array}$	(Madu and Agboola, 2018)
Saccharomyces cerevisiae	H2SO4 (0.5–2.5 %) for 30 to 90 min	cellulase 40 FPU	>7.0 mg mL-1 after 2 h of fermentation	(Lamb et al., 2018)
Klebsiella oxytoca ATCC1318	2 % (v/v) KOH	α-amylase	$50.91\pm1.27~\text{g/}$ L	(Tiwari et al., 2022)
Pecoramyces sp. F1 and Z. mobilis ATCC 31,821	-	xylanase	0.32 g ethanol/ g glucose	(Li et al., 2022)
Saccharomyces cerevisiae KCTC 7906	1.5 M NaOH at 80 $^{\circ}\text{C}$	cellulase	$\begin{array}{l} 29.9 \pm 1.8 \text{ mg/} \\ \text{mL} \end{array}$	(Song, 2024)

opposed to the conventional process, resulting in the elimination of associated costs, sustainability, and time saving as only 4 days are required to obtain ethanol from lignocellulosic biomass compared to 6–8 days for the conventional process.

Distillation

Traditional distillation systems rely on the opposing current of vapor-liquid mass transfer. Distillation recovers diluted volatile compounds, particularly ethanol, from the contaminated biomass streams. Fermented ethanol contains contaminants and is present in small amounts. In the process of distillation, bioethanol was extracted through the components of the blend. Rectification allows the ethanol to be condensed and purified. Dehydration allows the production of extremely pure (99.7 % by volume) ethanol (Singh et al., 2020).

Investigating differences in parameters of bioethanol production from rice husk

Pretreatment is a significant stage in the production of bioethanol and is also one of the most expensive stages. To find a solution to this issue, Ebrahimi et al. (2017) conducted a study to explore a new rice hull pretreatment method. They used acidified liquid glycerol as well as glycerol carbonate at temperatures of 130 °C and 90 °C for 1 h, respectively, and added cellulase as the hydrolytic enzyme for 72 h. The SSF procedure was carried out anaerobically by *S. cerevisiae* at 37 °C, with 5 % (w/v) glucan and a 10 FPU/g glucan of cellulase proportion. After three days of fermentation, the highest bioethanol yield was achieved, with 8.8 and 11.6 g/L for acidified liquid glycerol and glycerol carbonate pretreatment, respectively.

An investigation conducted by Cacua et al. (2019) aimed to assess the efficiency of alkaline pre-treatment and acid cellulase hydrolysis of rice husk for bioethanol manufacture using *S. cerevisiae*. The results showed that pre-treating rice husk with a 2.00 % w/v solution of NaOH led to a 43.24 % reduction in mass, with an average loss of about half when an acidic cellulase enzyme (CFB3S) was used to enzymatically hydrolyze the pretreatment RH samples. After 24 h of hydrolysis, the highest concentration of total reducing sugar was 7.788 g TRS/L. The obtained sugars were then prone to *S. cerevisiae* fermentation to produce a concentrate with a 3.7 % v/v concentration.

After examining the research conducted by Arismendy et al., (2020), the productivity of *Saccharomyces cerevisiae* IMR 1507 (SC 1507) and *Saccharomyces cerevisiae* IMR 1181 (SC 1181) was assessed through the

SSF method. The results demonstrated that although both strains generated a similar amount of glucose using ground husks (36.6 % for SC 1181 and 35.5 % for SC 1507), the latter was more cost-effective. Additionally, the SC 1507 yeast consistently performed better than the SC 1181 yeast. When comparing the SHF and SSF procedures utilizing SC 1181 yeast, the bioethanol yield was 35.3 %, while the SSF process yielded slightly more (38.2 %). The SSF process continued to increase over time, reaching 43.9 % for SC 1507 and 38 % for SC 1181 after 72 h.

The study conducted by Tiwari et al. (2022) utilized *Klebsiella oxytoca* ATCC 13,182 for the production of bioethanol from a lignocellulosic residue obtained from rice husk. The researchers used chemical, physical, enzymatic, and biological pretreatment approaches, including alkali, microwave, α -amylase, and *A. niger* pretreatment, respectively, to pretreat the rice husk. The highest yield of bioethanol was achieved through the chemical alkali pretreated rice husk, which had a conversion efficiency of 67.88 % for sugar and a bioethanol yield of 50.91 \pm 1.27 g/L. The biological pretreatment method using *A. niger* utilizing the submerged hydrolysate technique produced the second-highest bioethanol yield of 47.98 \pm 1.25 g/L with a utilization efficiency of 63.97 % for sugar.

Taghizadeh-Alisaraei et al. (2022) prepared bioethanol using a blend of orange peel and rice hull waste as their substrate. The substrate was pretreated and hydrolyzed using 3 % $\rm H_2SO_4$ at a temperature of 120 °C for 60 min, resulting in the release of glucose and arabinose. The yeast S. cerevisiae was added to the mixture at the proportion of 5 gs per kilogram of dry matter, and the fermentation process was carried out at 30 °C for 32 h. The resulting bioethanol content was 22.8 gs per liter.

Song (2024) demonstrated the importance of yeast strain and substrate selection in generating high bioethanol yields. After 48 h of enzymatic hydrolysis and fermentation, RH yielded 29.9 ± 1.8 mg/mL of bioethanol, achieving 85.4 % conversion rate. In addition, bioethanol (85.4 %) as well as lactic acid (92.5 %) had been effectively generated utilizing the rice husk hydrolysate. The quick consumption of glucose and the drop in xylose concentration show that S. cerevisiae converts efficiently. This study proved rice husk's considerable potential for use as biorefinery raw material, and it is anticipated that numerous base chemicals along with added-value goods can be created utilizing Rice husk.

Conclusion

This investigation explores the potential of rice husks as a source for biofuel production, highlighting the demand for alternative energy production against a background of concerns regarding the environment and rapidly depleting fossil fuel resources. Biofuels composed of biomass can substantially reduce emissions of greenhouse gases while increasing the reliance on renewable resources for a sustainable alternative. Biofuels have progressed throughout four generations in terms of taking advantage of biomass resources, enhancing long-term viability, and increasing the effectiveness of conversion. Rice husk is a secondary product of rice milling which is an abundant and underutilized feedstock for the production of bioethanol. Rice husks along with other lignocellulosic materials can be employed to efficiently produce bioethanol, a well-known biofuel. The production of bioethanol includes processes such as pretreatment, hydrolysis, fermentation, and distillation. However, further research is required to overcome constraints regarding technology and economic viability while increasing bioethanol production efficiency and scalability. Improvements are to be made particularly in the pretreatment techniques for making bioethanol production a truly sustainable alternative both environmentally and economically. By addressing existing obstacles and taking advantage of substantial lignocellulosic biomass resources, the feasibility of rice husks as a sustainable biofuel source can be fully realized, substantially influencing global energy transition and environmental sustainability. Continuous research and technological breakthroughs are required to make the production of bioethanol more efficient, cost-effective, and

scalable. By tackling existing obstacles and capitalizing on substantial lignocellulosic biomass resources, we can pave the way for a greener and more sustainable energy future.

Author contribution

Sakshi Chavan- writing the manuscript

Debasis Mitra, Anuprita Ray- conceiving the idea, editing the manuscript

Declaration of competing interest

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Data availability

No data was used for the research described in the article.

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