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Review

Recent Trends, Opportunities and Challenges in Sustainable Management of Rice Straw Waste Biomass for Green Biorefinery

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Abstract: Waste rice straw biomass and its burning in open fields have become a serious issue of greenhouse gases emission and air pollution, which has a negative impact on public health and the environment. However, the environmental impact of burning this agro-waste can be mitigated by diverting it towards green biorefinery through the sustainable production of energy, biofuels, organic chemicals, and building blocks for various polymers. This will not only help to reduce the reliance on limited fuels and various chemicals derived from petroleum, but also help in the restoration of the environment in a sustainable manner through its complete utilization. To maximize the inherent conversion potential of rice straw biomass into valuable products, this agriculture waste biomass requires a comprehensive analysis and a techno-economic review for its sustainable management. This review article focuses on the sustainable management of rice straw waste biomass via innovative valorization approaches, as well as the opportunities and challenges encountered in this sector for meeting the demand of current and future green biorefineries.

Keywords: rice straw waste biomass; biofuels; biochemical; green biorefinery; sustainable management

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1. Introduction

Stubble burning has always been a significant contributor to atmospheric greenhouse gases (GHG) emission, the increase in environmental temperature, and climate change. Since industrial revolution, GHG emission has not only impacted the air quality, climate, and environment, but has also been held responsible for serious deterioration of human health [1]. The Indian economy is largely based on agriculture and its produce. Hence, with periodic crop cultivation cycles, various agricultural activities generate a large amount of agro-residual biomass as waste. These agro-industrial wastes possess tremendous goods-and-services-based social and economic potential. Unfortunately, due to the absence of far-sighted sustainable management goals and suitable technologies, millions of tons of stubble waste has been routinely burned, which, indeed, acts as an impetus for perpetual industry-assisted environmental diminution [2,3]. For example, the retuning of rice straw in soil improves and sustains a better physical, chemical, and biological potential for its fertility and overall agricultural productivity. Nutritional deficiencies in soil, plants, animal, and human beings have been noted to be a significant impact on climate change. Moreover, depending upon changing agro-climatic conditions as well as scarce availability of existing technological interventions of biomass valorization, there is a limit to carbon sequestration and mitigation of emissions generated from stubble burning, especially in rural India [4].

Rice is one of the important agricultural crops after wheat and corn in Asia as well as throughout the world [5]. In Asia, the Indian subcontinent constitutes a large proportion of rice cropping land in the form of the fertile Gangetic Delta and Punjab Plains. Therefore, many states in India, such as West Bengal, Uttar Pradesh, and Punjab, etc., ameliorated about 124 million metric tons of gross production of rice in the year 2021–2022 (https://www.statista.com/statistics, accessed on 1 October 2022). However, the cultivation and harvesting of rice crop generates a huge amount of stubble waste known as straw. According to some previous estimates, about 1.0–2.0 kg straw is generated from every kilogram of rice grain harvested. However, the exact estimation of generated rice straw remains largely in oblivion due to the in-field burning of most of the stubble residues by the farmers. Open field burning of rice straw increases GHG emission, and is also a contingent release of huge particulate matter into the environment. In India, about 0.05% of total GHG emission has been anticipated to be contributed by the surplus rice straw burning. It is reported that open burning and anaerobic digestion of rice straw produces 592 and 0.122 tons of CO_2, respectively, on an annual basis [6]. Rice stubble residue primarily constitutes either of rice straw or rice husk. The stems, leaves, and spikelets of grain-harvested rice represent straw. Traditionally, the grain-separated straw has been utilized as animal feed and fodder. Apart from that, rice straw has also been used as a raw feed stock for various industries such as paper and pulp and bio-production of organic fertilizers. The traditional utilities of rice straw as fodder, bedding for animals, mushroom cultivation, thatching, and packing, etc., remains minuscule, keeping in view the availability of humongous, i.e., approximately 300 million tons, of surplus straw biomass generated per year in India [7]. Notwithstanding the recent interventions in various biomass valorization technologies, e.g., biofuel and other secondary product generation from rice straw waste, a large proportion of this important stubble biomass is either ploughed into the cropping field or burnt in the open to ash [8].

In recent years, the concept of biorefinery-assisted conversion of biomass into a distinct array of products, as well as energy, has gained momentum. Several pilot scale facilities are available, and numerous research and development projects are on-going to create fully functional systems from crop-based residual wastes [9]. Through concatenation of these biorefineries with lignocellulosic biomass and other agricultural residues, development of biofuels for energy is an emerging enterprise [10]. Many researchers have recently reported on the potential of rice straw as a biorefinery substrate [4,5,8,10]. The available data provided information on potential applications of rice straw in bioenergy generation [11]. Harun et al. [12] emphasized composition, management, and the role in a circular economy in another study. Recently, Zhang et al. [8] reviewed the products synthesized from rice straw via steam explosion as well as technological advancements. Most of the existing literature mainly focuses either on bioenergy, biochemicals, or other bio-products. However, in the present review article, different aspects of rice straw for green biorefineries has been explored along with various opportunities and challenges associated with its sustainable management. This review article is an effort to provide an updated and comprehensive information about all the possible products from rice straw, so that this waste biomass can be diverted towards the zero waste green biorefinery.

2. Composition and Availability of Rice Straw

Every year, the Kharif season in India generates a huge amount of waste in the form of rice straw. Determination of chemical composition of rice straw is very crucial to plan its valorization by itself or in combination with other biomasses. However, the overall composition of this biomass sometimes disadvantageously varies according to variety, season, climatic conditions, and geographical locations where rice crop is cultivated. Apart from cellulose and hemicellulose, rice straw also contains a significant amount of lignin, silica, and other minerals. Chemically, rice straw predominantly consists of cellulose (32–47%), hemicellulose (19–27%), and lignin (5–24%) [5,10]. Lignin is an amorphous polymer having at least three aromatic alcohols, i.e., p-coumaryl, coniferyl, and sinapyl, as its structural constituent [13]. In plants, lignin does not exist as a solitary molecule; rather, it makes an amalgamation of a lignin–phenolics–carbohydrate complex to make the entire plant cell wall a highly robust system. However, rice plant maintains a great degree of heterogeneity in terms of cell wall carbohydrate: (63%)-lignin (27%)-uronic acids (2%)-acetyl content (4%)-trans-p-coumaric acid, and (4%)-trans-ferulic acid (~1%) [14]. Rice straw contains comparatively higher concentrations of esterified as well as etherified forms of p-coumaric acid and ferulic acids than corn and wheat. Apart from the cellulosic, hemicellulosic, and lignified cell walls, and despite being impoverished in nitrogen content, rice straw contains a redeemable amount of ash (>10%) that, overall, has high silica content, which is ~75% SiO_2, and <15% alkali content [15]. Rice is one of the early crops domesticated by the humans. Moreover, the links of rice, especially the domestication of *Oryza sativa*, have been mostly attributed to the Asian continent [16]. Quoting the words of famous archaeobotanist Dorian Fuller, "Asian civilization was built on rice-on *Oryza sativa*, to be exact", can be used to contest the ancestry of rice, and its probable domestication by Yangtze River valley dwellers in China sometime around 8000–10,000 BCE. However, the taming events of other more recent varieties of *Oryza* sp. such as *O. japonica, O. indica,* and *O. glaberrima*, etc., could be traced back to different time scales and places throughout the world. The two widely grown and contrastingly domesticated rice varieties are *O. sativa* (Asian origin) and *O. glaberrima* (African origin). Their domestication is a matter of great debate, but they are globally grown varieties [17]. Rice is one of the most important staple crops available almost around the globe, which indicates its essential importance in shaping humanity's history and present, as well as future. Rice acreage is expected to increase in the future, too, because of high productivity and government incentives for farmers, and there will also be an increase in its straw, which can be used as biofuel, agricultural fertilizer, or other value-added products through appropriate technologies.

3. Potential of Rice Straw as Green Biorefinery

Traditionally, waste biomass generated after the processing of rice was either burned or used for flooring and roofing, composting, animal feed, and some handicrafts [18], as mentioned in the introduction. However, modernization has changed all of the concepts, and over past few decades these residues were reported as a potential biomass for biorefinery. Biorefinery is an approach for meaningful utilization of biomass for the production of marketable value-added products [19]. The biorefinery designs have a sequential line. The first step is to address social demands and the possible application of products, followed by the identification of the molecular structure of the derived chemicals and the designing of reaction pathways for the maximum synthesis of the desired products. The most important step in this process is the selection of suitable feedstock for the synthesis of the maximum numbers of chemicals. Solid, gaseous, and liquid biofuels, fine chemicals, organic acids, and biopolymers are mainly reported from carbohydrate rich biomass feedstock [18–20].

Pyrolysis of biomass is the process mainly used to generate all kind of fuels, i.e., solid (bio-char), liquid (bio-oil), and a mixture of light gases (syngas), from these residues [15]. In addition to this, certain other valuable products can also be produced using rice straw, such as proteins, enzymes, and alcohols (through microbial fermentation), biocomposits, biocompost, biocoal, biohydrogen, furfurals, lactic acid, biogas, biofoam, wood additives, bioinsecticides, and many more, as shown in Figure 1. However, the yield and concentration of these various end products are highly influenced by the typical process and its parameters [19].

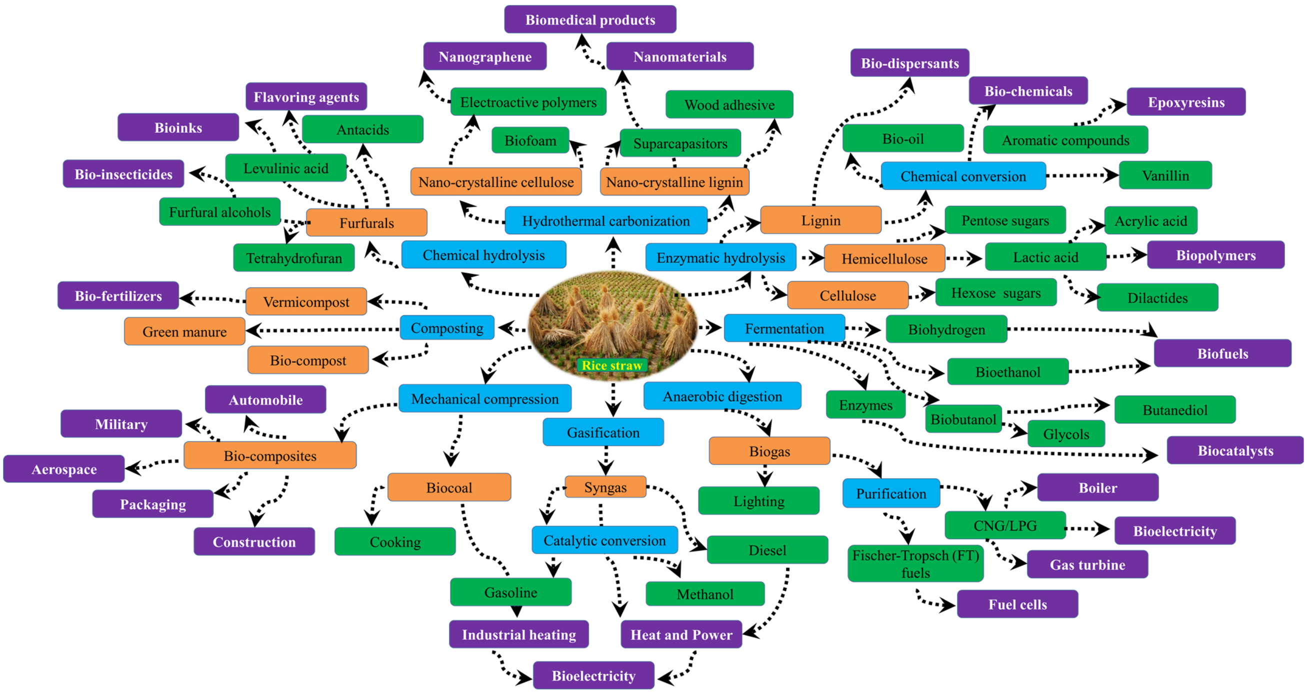

Figure 1. Potential value added products from rice straw biorefinery and their applications.

In biorefineries, rice straw was reported to be used for the production of renewable fuels, especially the second-generation biofuels [15,19]. As mentioned in the compositional section, rice straw mainly consists of cellulose, hemicellulose, and lignin, and based on this, a variety of biofuels can be synthesized using this biomass. Song et al. [20], in a study, reported biogas production from rice straw using an anaerobic digestion approach. The potential of rice straw as a feedstock for the production of bioenergy increased in past few decades, and, since then, a number of studies have been conducted to confirm the above said statement [12,18,20]. Dash et al. [21] studied the effectiveness of rice straw as biomass for production of bioenergy. In another study, Takano and Hoshino [22] used rice straw as a feedstock for the production of ethanol using a fungal species *Mucor circinelloides*. In a study conducted by Idris and Hashim [23], the potential of rice waste as a feedstock of choice in biorefineries was evaluated. Similarly, there are reports for the production of composite from rice straw [22,23]. In a recent study, Harun et al. [12] also highlighted the potential of rice straw in biorefineries and its utilities.

4. Biorefinery Based Value Added Products of Rice Straw

Biorefinery is a collective term for sustainable utilization of biomass and its processing and eco-friendly conversion into a variety of marketable goods and valuable products. The process has become more viable economically and environmentally as most of the derived products have reduced carbon footprints. Similarly, as stated above, the rice straw waste also has great biorefinery potential, and major products synthesized from rice straw have been described below, and are also summarized in (Table 1).

Table 1. Important biorefinery products produced using rice straw biomass and their applications.

Product	Bioprocess	Application	References
Biogas	Microbes breakdown the organic matter to gases, mainly methane	Cooking, heating furnaces, boilers	[24]
Composting	Aerobic digestion of complex organic matter by microorganisms into simpler substances	Reduced environment burden and enhanced soil fertility	[25]
Electricity Generation	Sequential oxidation of organic matter to ATP, where a terminal electron acceptor accepts the electrons to produce electricity (current)	Reduces environmental pollution caused by burning of paddy straw, and utilization of water for synthesis of electricity and generation of power for industrial and domestic usage	[26]
Pellets and Briquettes	Biomass is compacted into highly dense fuel	Water boilers, stoves, furnaces, and biomass-based power plants	[27]
Bio Char	Pyrolysis, gasification, and hydrothermal carbonization of biomass	Bioremediation of contaminants from soil and water, and improves soil quality	[28]
Bioethanol	Hydrolyses and fermentation	Transportation fuel blended with gasoline, sterilizing agent	[29]
Bio-CNG	Anaerobic digestion of biomass	More combustible than diesel, produces less noise pollution, less emission of CNG, produces fewer toxic products	[30]

4.1. Biogas

Straw biomass, especially rice straw, is considered to be one of the most suited feedstocks for the production of liquid or gaseous biofuels as they are rich in carbohydrates. The sugars can be easily extracted from biomass by enzymatic action and converted into liquid/gaseous biofuels via fermentation, anaerobic digestion, or gasification [31]. Methane, ethanol, and biogas are some of the biofuels produced using rice straw feedstock. Anaerobic digestion is generally preferred for the production of methane from rice straw. However, the presence of lignin in its complex structure makes its degradation process a bit difficult during anaerobic digestion. The major limitation in biogas production is carbon–nitrogen (C/N) ratio [32]. It has been observed that microorganisms consume carbon faster than nitrogen, and the C/N ratio must be in the range of 20–30 (*w*/*w*). If the C/N ratio is not in the optimal range, then the biodegradation of the complex rice straw structure is improper, which ultimately hampers the production of biogas [33,34]. In order to overcome this disadvantage of anaerobic digestion, researchers have recently improved it through pretreatment of rice straw. Various pretreatment methods, i.e., steam explosion, acid-base hydrolysis, photocatalytic degradation, and many more strategies have been employed to break the complex structure of rice straw [9,35]. These methods have degraded the biomass to varied degrees. In a study, Xu et al. [36] used straw biomass for the production of methane and observed that there was an increase in the yield of methane when rice straw was subjected to pretreatment prior to anaerobic digestion.

4.2. Composting of Rice Straw

The role of composting in the circular economy was modeled over 25 years ago. Initially, compost was prepared by stock curing of biomass and animal dung in static heaps and pits. Composting is an ancient practice, and it takes more than one hundred days [37]. This practice is grossly inadequate for managing the millions of tons of surplus biomass being generated in mechanized high-tech farming. Windrow technology composting, turning or in vessels, consists of air circulation and moisture control, as well as adding nitrogen, microbes, and enzymes, and has a cycle of about 40 days [38]. However, requirements of space or land, the long composting cycle, the release of GHGs, and supply chain logistic add some challenges in the management of rice straw through this approach. However, these challenges can be overcome through scientific interventions to make it a cost effective and sustainable strategy.

Composting of bio-mass leaves behind about 40–45% manure on a dry weight basis, and the rest is water and easily decomposable carbon, which gets released into environment in various forms of gases, smells, and other volatiles [39]. In a study, Jusoh et al. [25] used rice straw as a major component for composting and observed that mixing of biomass with dung increased its degradation efficiency. In another study, it was suggested that the utilization of rice straw for composting is an effective way to generate revenue from this agriculture waste [40]. Nghi et al. [41], in a study, compared the potential of rice-straw-based compost with organic fertilizer to study its effect on potato yield and observed that rice-straw-based compost enhanced the yield similar to that of organic fertilizer. Similarly, Ma et al. [42] also used rice straw as a major component of compost. It was also observed that the addition of 1% amino acid to rice-straw-based compost increased its nitrogen content by 67%.

4.3. Electricity Generation

To generate electricity from rice straw, the most important step is availability and moisture content of raw material. A straw-to-grain ratio was used to determine the maximum availability of raw material, and it was nearly 0.75 [43]. It was also reported that the rice straw with low moisture content generates high power. Thus, to reduce the moisture, the biomass was dried to constant weight in sunlight before processing [44]. Suramaythangkoor and Gheewala [45] reported that every 13% increase in moisture content reduces the power generation yield by 2%.

In 2006, Punjab became the first state to witness the first rice-straw-based power plant. It is situated in the Jai Kheri Village of Patiala district of Punjab. This power plant has an operational capacity of 10 MW, and 70,000 tons of rice waste was used for this purpose annually [43]. Hassan et al. [26], in a study, used rice straw for the production of electricity using a microbial fuel cell (MFC) and observed 145 mW/m^2 with 1 g/L concentration of biomass in a dual chamber MFC. The cellulose degrading bacteria were used as a biocatalyst for this process. Darmawan et al. [46], in a study, also evaluated the potential of rice straw for the generation of electricity and observed a 43% enhancement in power generation after optimization of different process conditions.

4.4. Pellets and Briquettes

Making pellets and briquettes consists of chopping, drying, densification, and binding the loose straw with adhesives [27,47]. In the manufacturing of pellets from biomass, the crushed biomass was pressed to increase its density and to create smaller sized pellets. These pellets were used as biocoal, which are easy to store and transport, and have high efficiency in comparison to fossilized coal [48]. This biocoal find its uses in water boilers, stoves, furnaces, and biomass-based power plants for the production of heat and electricity. Use of these pellets and briquettes as biocoal in improvised stoves considerably reduces smoke and particulate matter pollution in the domestic as well as commercial sectors [49].

4.5. Biochar

Heating of straw or bio-mass at 300–600 °C in the absence of oxygen yields solid residues called biochar, a condensate called bio-oil, and a non-condensate used as biomass for heating purpose [50–52]. The biochar is made up of the recalcitrant constituent of biomass, which is cellulose and lignin. Generally, it leaves 30–35% of recalcitrant carbon and lignin, which can stay for hundreds of years in the soil and sequester carbon. This recalcitrant fixed carbon loses its weight, volatile contents, and density, and calorific value increase with temperature at the cost of moisture and other elements [52]. The fate of the rest of the feed stock lost in the process and the carbon footprint must be traced during the process.

The nutritional value of biochar is low, but it improves the physico-chemical properties of soil and increases moisture retention, which enhances microbial activity and diversity in the soil in addition to their efficient utilization of fertilizers by plants [53]. In a recent study, Sakhiya et al. [54] used rice straw for production of biochar at 400–600 °C and further used this biochar for degrading heavy metal contamination of drinking water. In a similar study, biochar was used to degrade soil contamination to enhance its reclamation and agricultural potential [28]. Foong et al. [55] also synthesized biochar from rice straw at elevated temperature and used it for remediation of waste water. Mei et al. [56] synthesized three different types of biochar from rice straw by pyrolysis at 300, 500, and 700 °C and used this for absorption of copper from aqueous solution as well as for removal of heavy metals.

4.6. Bio-Ethanol Production

The ethanol policy of India was made as early as the 1950s. Ethanol could be blended into petrol and marketed by all 63,000 petrol pumps in the country. Surplus or spoiled grains, starches, molasses, corn, sugar beet, yam, and sugarcane juices were the preferred feed stocks for ethanol production with the first generation technologies. However, it competes with the policy of food security, especially in densely populated countries such as India. All out efforts are being made to develop technologies for ethanol production from surplus ligno–cellulosic waste biomass from agriculture and related sectors [57–59]. To extract fermentable sugars from rice straw biomass, it was first pretreated and the sugar hydrolysate was further fermented to ethanol by microbial fermentation [60]. Takano and Hoshino [22], in a study, produced bioethanol from rice straw by simultaneous saccharification and fermentation using a fungus *Mucor circinelloides*, and observed 30.5 g/L ethanol after 35 h of incubation. Besides rice straw, other carbohydrate-rich waste biomass has also been reported from production of ethanol, i.e., rice straw, rice bran, wheat straw, wheat bran, sugarcane bagasse, pine needles, corn cobs, corn straw, corn stover, etc. In a recent study, Suri et al. [30] reported bioethanol production from C5 sugars extracted from pine needle biomass. The biomass was pretreated with xylanase of *Bacillus* sp. XPB-11.

4.7. Bio CNG Production

2G technologies of lignocellulosic raw material is the major focus of current R&D, investments and policies. Bio CNG is the cheapest energy source, giving 52,000 kilojoules per kilogram of calorific value, which is approximately 167% higher than biogas [61,62]. Emissions of bio CNG contain the smallest concentrations of carbon monoxide (CO), hydrocarbons, nitrous oxides (NOx), and suspended particles, and are relatively much safer as compared to other fuels. CNG, being more combustible than diesel, produces less noise pollution. Emissions from bio-CNG fueled vehicles are much safer since they have significantly lower concentrations of toxic elements such as carbon monoxide, nitrous dioxide, and particulate matter [63]. Similar to biogas, bio-CNG can also be synthesized using anaerobic digestion of rice straw. This can be used as an energy fuel for cooking, heating, cooling, vehicles, and electricity brackets. Rice straw biomass has immense economic potential as substrate for the production of CNG [64].

4.8. Biobutanol Production

Just like bioethanol, biobutanol is another alternative fuel to non-renewable fuels. It is reported to have better energy efficiency than bioethanol because biobutanol has 30% higher energy content, low vapor pressure, is less flammable, has less sensitivity to water, and is less volatile [59]. It is generally produced under strict anaerobic conditions using anaerobic bacteria such as *Clostridium acetobutylicaum* and *C. beujerinckii*. Biobutanol has gained interest in the recent past and can be synthesized from both agro-residues and lignocellulosic biomass. Vivek et al. [65], in a study, reported on biobutanol from rice straw and also explored its possibilities as an alternative fuel, as well as the challenges associated with its production. Dutta et al. [66] also used rice straw as a feedstock for biobutanol production and reported 28 kg biobutanol from 100 kg of biomass. Production of these biofuels from biomass is an ABE fermentation process in which acetone, butanol and ethanol are produced simultaneously [67]. This is a promising technology for the sustainable utilization of biomass to biofuel, but there are certain challenges associated with this process. A major challenge is the production of by-products such as furfural, hydroxy-furfurals, and ferulic acid [68,69].

4.9. Biocomposites from Rice Straw

Biocomposites were generally made using wood chips and wood blocks. However, increasing scarcity of wood, environmental concerns, and competition have provided a great opportunity for using different waste alternatives for the production of biocomposites [70]. Strawboard is one of the most common biocomposites produced using biomass. Production of strawboard is a win–win opportunity in which lignocellulosic biomass is pre-treated with supercritical CO_2 that enhances the value of fiber and reduces the cost. Similarly, high-quality straw powder/polylactic acid biocomposites were produced from this biomass [71]. In addition, this biomass was also reported for the production of paper/pulp. It was observed that use of residues reduces the pressure on forests caused due to extraction of wood for paper making. It was also reported that de-waxing of fibers prior to paper making adds value to the process, as wax can be used as a resin for other applications [72].

4.10. Production of Enzymes

Enzymes are biological catalysts and the backbone of many industrial processes. These biocatalyst speeds up the biological reactions that occur during synthesis of metabolic products. The major limitation in the production of enzymes is their cost due to the costly substrate generally used for their production. This can be overcome by using low-cost lignocellulosic waste biomass as a substrate for enzyme production. The major enzymes produced using these residues are cellulases, xylanases, ligninases, pectinases, and amylases [73]. Synthesis of enzymes using biomass not only reduces the overall cost of enzyme processing but also reduces the environmental pollution caused by unmanaged biomass. The carbohydrate entities of biomass act as a substrate for energy, growth, and metabolism, and thus the enzyme production. Microbes use these enzymes for depolymerization of complex carbohydrates into simple sugars which are subsequently fermented into various valuable chemicals and bioenergy products [74]. In a recent study, rice straw was used as a substrate for the production of cellulose-free xylanase from *Tricoderma* sp. under solid state fermentation [75].

5. Rice Straw Components Derived Biochemical

The major constituents of plant cell walls are cellulose, hemicellulose, and lignin, as mentioned above. These constituents are resistant to degradation and need to be pretreated. Various chemical (acid, alkali), physical, mechanical, and enzymatic methods have been proposed that can be successfully used for the effective conversion of complex biopolymers to monomeric units [76,77]. These monomeric subunits can also be used for the synthesis of useful chemical derivatives. The detailed list of chemical derived from cellulose, hemicellulose, and lignin, along with their possible applications, is discussed in the next section and is also summarized in Table 2 and Figure 2.

Table 2. Different chemicals derived from rice straw and their applications.

Major Constituents	Chemical Derivatives	Application	References
Cellulose	Nanocellulose	Nanocrystalline cellulose is used as a filler in foods and pharmaceuticals, enzyme immobilization, and antimicrobial and medical materials	[78]
	Cellophane	Used in food packaging as a transparent sheet with low permeability to air, oils, bacteria, water	[79]
	Cellulose acetate	It find its uses in a wide variety of applications, including fibers, plastics, photographic films, lacquers, and reverse osmosis or dialysis membranes	[80]
	Oxycellulose	Important cellulose derivative for a variety of cosmetics, such as anti-acne cream, lotion, and sunscreen, and pharmaceutical and agricultural products.	[81]
	Microcrystalline cellulose	Microcrystalline cellulose synthesized from various processes such as reactive extrusion, enzyme mediated, steam explosion, and acid hydrolysis.Used as an emulsifier and stabilizer, anticaking and dispersing agent.	[82]
	Textile, paper and cardboard production	Suitable for packaging as corrugating medium, wrapping, and insulating board. Composites formed from rice straw modified by in situ polymerization of ammonium polyphosphate polyelectrolyte and high-density polyethylene have been used as materials with good flame retarding properties.	[83]
Lignin	Lignosulphonate	Used as a hydrophobic for concrete admixtures, production of brick or tile, oil well drilling fluids, and dispersion of pigments, retarder for oil well cementing.	[84,85]
	Eugenol	Eugenol (4-allyl-2-methoxyphenol) is an allyl chain-substituted guaiacol, a member of the allylbenzene class of chemical compounds. It is the active ingredient in clove oil and has emerged as an anesthetic used by hobbyaquarists. It is also used for laboratory zebrafish, including mutagenesis protocols, antioxidants, and as a pharmacological compound	[86]
	Organic acids (lactic, acetic and citric acid)	Used as food aciduvalant and preservative that helps in preventing food spoilage caused by microbes	[87]
	Vanillin	Flavouring agent in food industry, additive in perfumery. Antioxidant, antifoaming potential, vulcanization inhibitor and chemical precursor for pharmaceutical and agrochemicals industries	[88]
	Ferulic acid	Due to its strong antioxidant properties, FA can be utilised as a preservative in the food sector. In addition to its use as a food additive and a cosmetic ingredient, FA is known to have anti-diabetic, anti-cancer, neuroprotective, and cardiovascular properties. In induced diabetic rats, FA significantly lowered blood glucose levels or minimized the physical effects of diabetes (such as obesity).	[89]
Hemicellulose	Xylitol	Employed in pharmaceutical and thin coating applications as sugar-free sweeteners for diabetic patients and chewing gums. Additionally utilised in dental applications such as mouthwash, tooth hardening, as an antibacterial agent, and toothpaste compositions.	[90]
	Xylans	Food coating, biomedical applications, and packaging films all have potential uses of xylan. It is an emulsifier and protein foam stabiliser in the food sector, as well as an adhesive, thickening agent, and an additive for plastics.	[91,92]
	Xylose	Xylose is used as a sweetener in food and beverages because of its anti caries properties. It is an attractive sugar because it can be converted to ethanol and furfural. In addition, it is used as a diagnostic agent to observe malabsorption.	[93]
Ash	Silica	It can be used as cementing material and a raw material in bioremediation and clinical procedures	[94]
	Nano-silica	Fertilizer to enhance crop production	[95]

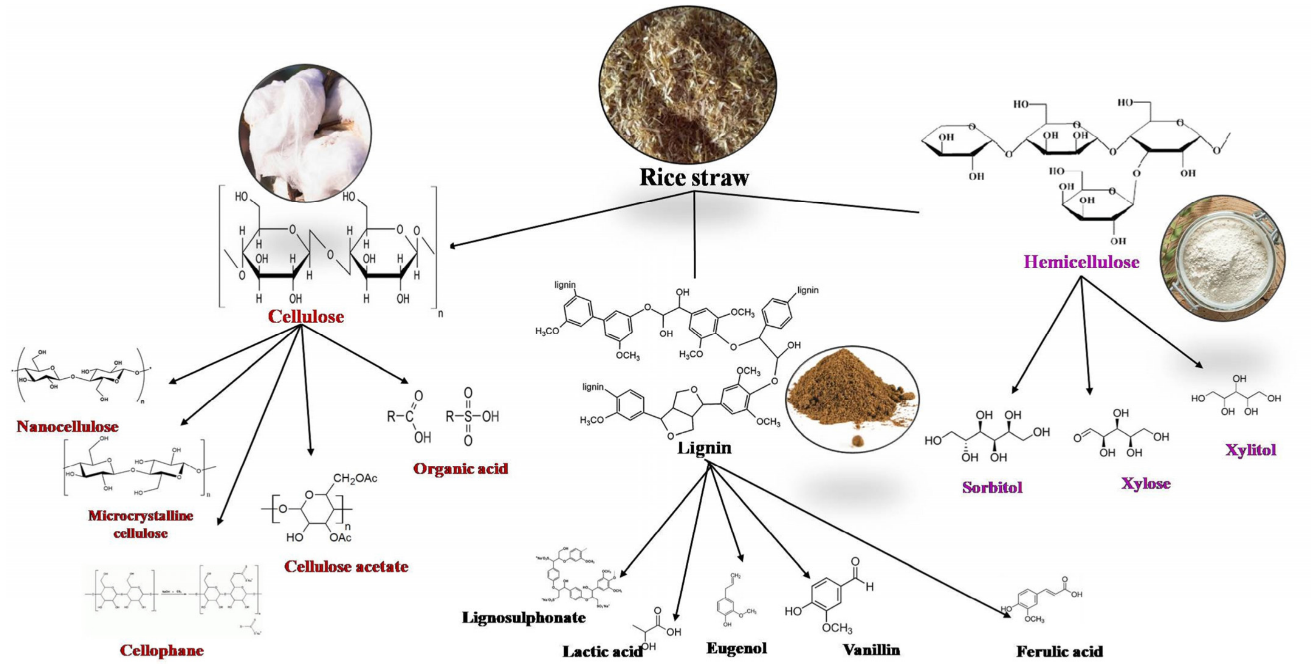

Figure 2. Chemical derived from different constituents of rice straw biomass.

5.1. Lignin

The depolymerization of the complex structure of lignin into small monomeric molecules, using advanced techniques, is necessary for the synthesis of valuable chemicals and the maintenance of carbon balance, as well as for energy and fuels production [96]. Thermochemical depolymerization of lignin empowers the production of low molecular weight compounds, i.e., vanillin, eugenol, lignosulphonates, hydroxylated aromatics, aldehydes, aliphatic acids, and many others. The most commonly used method is base catalyzed depolymerization (BCD), which has been widely studied for procurement of phenolic monomers based on the heterolytical cleavage of the (β-*O*-4) ether bond, the most common (60%) linkage in lignin [97]. However, certain other organic acids such as lactic acid, acetic acid, citric acid, etc. have also been synthesized using lignin rich residues. These organic acids find their applications in the food processing industry as acidulates or preservatives that protect the food from microbial spoilage [98]. Lignosulphonate is a lignin-derived product that is insoluble in water and is used as a tanning agent in the leather industry. This tanning sulphonate was extracted from rice straw and used to tan leather in one study [99]. According to one study, sulphonation of lignin increases its efficiency and allows it to be used as a cementing material in the cement industry as well as in the dying industry [100].

5.2. Hemicellulose and Cellulose

These components of rice straw are made up of C6 and C5 sugars and can be fermented into desired biochemicals by the action of microorganisms. Hemicellulose can be broken down into its monomeric units such as arabinose, xylose, mannose, galactose, ribose, lyxose, etc., which are amorphous in nature and can be used for the synthesis of valuable chemical derivatives such as xylitol, 5-aminovalaric acid, 1,5-diaminopentane, itaconic acid, levulinic acid, etc., which were well reported from hemicellulose [97]. The xylitol and xylose are two main sugar free sweeteners extracted from hemicellulose that find uses in chewing gums, pharmaceuticals, and mouth washes. The most abundantly present carbohydrate polymers include C6 sugars, i.e., glucose, mannose, and galactose subunits. This is different from starch only in the configuration and arrangement of bonds formed between glucose units. Cellulose can be degraded to its monomeric units by the action of microbial enzymes. A variety of organic acids have been reported from the fermentation of these complex sugars, including acetic acid, ferulic acid, lactic acid, formic acid, succinic acid, malic acid, levulinic acid, aspartic acid, and many more. These acids were well reported for anti-diabetic, anti-cancer, neuro-protective, and anti-oxidant activity [101,102]. Other phenolic (p-hydroxy benzoic acid and vanillin) and polyphenolic compounds (glycerol, xylitol, arabitol) were also reported from rice straw. The phenolic additive, especially vanillin, is a flavoring agent used in the food and perfumery industries [103].

Nanocellulose is also an important chemical derivative synthesized from cellulosic fiber of leftover agricultural residues. It is cellulose having size of 100 nm. It is a promising alternative as a packaging material in food and pharmaceuticals, having promising anti-microbial activity, a low thermal expansion coefficient, a highly crystalline nature, low toxicity, great optical properties, and high biodegradability potential. The –OH group in nanocellulose facilitate its functionality. Based on shape and size, it is generally classified as cellulose nano-fibers (CNF), nanocrystals (CNC), and bacterial nanocellulose (BNC) [78]. Microcrystalline cellulose is also a cellulose derivative synthesized using various processes such as reactive extrusion, enzyme mediated steam explosion, and acid hydrolysis. It is also called refined/powered wood pulp, which finds use as an emulsifier, stabilizer, anticaking, and dispersing agent. The chemical composition of microcrystalline cellulose is similar to that of cellulose; it only varies in physical appearance that adds an extra property to dissolve in water easily [79]. Similarly, oxycellulose is another such cellulose derivative, generally synthesized by oxidation of complex cellulose. Oxidation of cellulose results in conformational changes in the structure and alters its physical as well as chemical properties. It has applications in the cosmetic industry as an anti-acne cream, lotion, sunscreen, pharmaceutical, and agricultural product. It is non-toxic in nature and exhibits anti-bacterial properties [104].

5.3. Ash Content

Besides lignin, cellulose, and hemicellulose, other major constituents produced by pyrolysis of waste biomass is ash. The concentration of ash may vary with harvesting time, environment, and geographical location of the field, but, in general, rice straw consists of 13–20% ash [105]. Processing of rice straw in biorefineries for production of value added products sometimes leaves semi burned residues in the form of ash. The ash is considered to be waste, but researchers in the past have reported that rice straw ash is rich in silica, which is a stable composite, chemically as well as thermally, and can be used as cementing material [104]. In the past, silica has been extracted from the waste produced during the processing of rice straw and it has also been reported that it is an important inorganic chemical that can be used as raw material in bioremediation, clinical procedures, and the cement industry [94]. In a study carried out by Sayed and El-Samni [105], it was reported that rice straw ash is a good substitute for cement. It was further reported that silica-rich waste ash has a higher compressive strength as compared to other tested cementing materials. In another study, rice straw waste was burned at higher temperatures and processed to form nano-silica [106]. Wibowo et al. [95], in a study, used a sol-gel extraction method for the extraction of silica from rice straw to produce silica nanoparticles (Si-NPs),which were used as fertilizers to enhance production of tomatoes, peanuts, and soybeans.

6. Bio-Economic Analysis of Rice Straw Biorefinery

Waste biomass is now viewed as a valuable resource that can supplement petroleum feedstock to a large extent if used properly to structure the bio-based economy. It is critical to define the investigated system and its limits in order to conduct a thorough study of the value chain in rice-straw-based biorefineries. The majority of biomass-based biorefineries are primarily focused on the production of second generation biofuels, particularly ethanol. However, a biorefinery concept is being developed to improve its bio-economics and sustainability by producing all possible valuable products from available waste biomass [107]. Separate hydrolysis and fermentation; hydrolysis and generation of furfurals by fermentation of sugars; separate hydrolysis and co-fermentation; separate fermentation and synthesis of biochemicals by lignin liquefaction and fermentation of cellulose; synthesis of furfurals from hemicellulose; and synthesis of chemicals from lignin [12,108] are the five strategies for rice straw biorefinery processes.

It has previously been reported that co-fermentation lowers the overall production cost of a biofuel biorefinery [109]. The production of co-products during biomass processing reduces costs and makes the process more environmentally friendly. A similar study found that producing bioethanol alongside other chemical byproducts lowers the overall cost of the process. This process produces high-value chemicals such as catechol, acetic acid, formic acid, ferulic acid, acetaldehyde, phenols, and others [110]. Based on previous techno-economic studies conducted by Jarunglumlert and Prommuak [111], it was concluded that co-production strategies aid in lowering the minimal selling price of bioethanol to near market price, implying the possibility of industrializing bioethanol production as a significant substitute for fossil fuels.

Open field burning of rice straw causes pollution and environmental problems, but it can be converted into valuable products such as biocoal, which can produce bioelectricity in power plants. Initially, rice straw was used to make bioethanol, but this concept failed to meet the criteria for a sustainable and cost-effective biorefinery. Rice straw should be diverted to a range of products rather than only one product [112]. Thus, it can be simulated from the available literature that technological advancements can aid in the reduction of total processing costs, the production of high value co-products, and the reduction of environmental burdens in order to develop a cost-effective zero-waste biorefinery for rice straw. By creating a waste biomass-based bioeconomy, through production of various products, will help in waste management, wealth generation, and environmental protection, in addition to creating various job opportunities.

7. Challenges Associated with Rice Straw Bio-Refining

A number of researchers have suggested various sustainable and environmentally ecofriendly strategies for utilization of rice straw waste for valuable products through green biorefinery [15,17,25,42]. However, during processing of biomass using recent technological interventions, some GHGs are still stimulated and aggravated, which can be converted into commercial CNG. Complete utilization of rice straw has certain hurdles, as given below, which need to be addressed before the commercialization of any straw-based product. The major challenges and possible solutions for these have been summarized in Table 3.

Table 3. Challenges associated with complete utilization of paddy straw for biorefinery and their possible solutions.

Challenges	Solutions	References
Large amount of ash and alkali metals, which is corrosive in nature	Ash can be used as cementing material	[57,60,63,65,67,68]
Harvesting time, chemical fertilizer reduces the quality of raw material	A proper system for time and processing can be maintained.	
Excessive use of chemical fertilizers reduces the nutritional composition of soil	Use of composting and vermicomposting reduces the chemical burden of soil and also enhances its nutritional value	
Production cost associated with processing of raw material	Easy and on-site availability of biomass	
Generation of greenhouse gases	Gas produced can be compressed to CNG to be used as fuel	
High moisture content	On-site drying using combustion and heat boilers reduces the moisture content, enhances the density of material, and ultimately reduces transportation and logistics cost	
Complex structural composition	Pre-treatment of biomass before processing	

- Large amounts of ash and alkali metals are produced during thermal and chemical processing of rice straw which are corrosive in nature. Furthermore, formation of slag during the combustion process can corrode boilers and heaters, and hamper their overall working and functioning. However, utilization of this ash and slag as cementing material can solve this problem and can compensate the cost of the process [77,103].

- The timing of harvesting also affects the characteristic composition of raw material as the insect pests degrade the straw and affect the quality of raw material. This problem can be solved by maintaining a proper system for timely harvesting so that all the material used for various technological interventions has the same chemical composition from which to obtain high quality value-added products and biochemicals [15].
- The constituent composition of rice straw was also affected by continuous use of chemical fertilizers. The fertilizers can be replaced with rice straw compost, organic manure, and biofertilizers that will not only help to improve the quality of the rice crop and straw and reduce the use of costly chemical fertilizers, but that will also enrich the soil with humus and suppress the diseases caused by insects and pests [19,113].
- The raw material and its value chain logistics constitute 30 to 40% of total production cost. The process must be established for proper collection, processing (drying, chopping), and transportation of raw material to reduce the logistics costs. The raw material must be pressurized into small pallets which can be easily transported and can help to reduce the cost, which was observed by various earlier researchers for a sustainable biorefinery [114].
- Drying is an important parameter for the processing of biomass in biorefineries, especially during the recovery of bioenergy from the biomass. However, the use of solar radiation and its allied natural renewable technologies can be beneficial to remove the moisture content at lower cost. The transportation of raw material after drying can reduce the time, transportation, and other logistics costs [115].
- Use of super critical (CO_2) methods for compositional extraction and other clean technologies for the rice straw are expensive at the commercial level. However, with these technologies, the compositional fractions obtained will be superior in terms of quality and quantity which can be further transformed into all possible products through scientific interventions and innovative biorefinery techniques to manage the overall cost of this green biorefinery in a sustainable manner.

8. Conclusions and Future Perspectives

Millions of tons of rice straw are available as surplus biomass around the globe, with abundance in Asia, as rice is the most commonly cultivated staple crop in the Asian continent. Rice straw burned in open fields pollutes the air and causes respiration-related problems; however, this agriculture waste biomass can be diverted to potential bio-energy products and other value-added biochemicals through scientific interventions when the agriculture sector is facing several challenges. The concept of a green biorefinery is a new approach that has been developed from the available knowledge and competences as well as innovative solutions through the amalgamation of various technologies. Thus, complete utilization of rice straw as feedstock for production of value-added products in green biorefineries using new innovative technologies and biotechnological interventions is the need of the hour for the recovery of bioenergy and biochemicals in a sustainable manner. Furthermore, rice straw management through the green biorefinery and zero-waste technologies, as discussed in this article, must be implemented at the ground level in order to improve soil fertility and obtain the renewable sources of bioenergy, valuable biochemicals, and financial and economic benefits to all stakeholders, in addition to endless benefits for the environment.

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