



Contents lists available at ScienceDirect

Journal of Bioresources and Bioproducts

journal homepage: www.elsevier.com/locate/jobab

Utilization of waste straw and husks from rice production: A review

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ARTICLE INFO

Keywords:

Rice straw
Rice husk
Bioethanol
Biogas
Adsorbent
Silica
Cellulose
Lignin

ABSTRACT

As a staple food for much of the world, rice production is widespread. However, it also results in the generation of large quantities of non-food biomass, primarily in the form of straw and husks. Although they have been little utilized and much rice straw is still simply burned, these ligno-cellulosic materials potentially have considerable values. This review considers the composition of rice straw and husks, the various processes involved in the production of valuable products, and a range of uses to which they can be put. These include agricultural amendments, energy production, environmental adsorbents, construction materials, and various speciality products.

1. Introduction

1.1. Rice production and waste biomass

Rice is the staple food for much of the world's population, especially in Asia and Africa, but its annual production generates huge quantities of straw (estimated as $\sim 8 \times 10^{11}$ kg by Domínguez-Escribá and Porcar, 2010) and husks ($\sim 1.5 \times 10^{11}$ kg by Singh, 2018). Currently, only $\sim 20\%$ of rice straw is used for practical purposes, such as production of biofuels, paper, fertilizers and animal feed, and after harvest most is either burned in situ, incorporated in the soil, or used as mulch for the following crop (Hanafi et al., 2012). However, straw incorporated into the soil degrades slowly and can potentially harbor rice diseases, whereas burning is becoming socially unacceptable because of extensive atmospheric pollution (Kadam et al., 2000), including greenhouse gas emissions (Arai et al., 2015) as well as smoke.

Efforts are being made to develop economic and socially acceptable uses for agricultural waste, and as reviewed by Moraes et al. (2014), use can be made of all of the materials from the rice production cycle. Of the various so-called waste products, broken rice and rice bran can be fully utilized by the food industry, and are not considered in the present review, although it is worth pointing out that rice bran has potential applications as a functional food through its ability to inhibit colonization of *Salmonella* in the gastrointestinal tract (Bodie et al., 2019), as well as being a source of oil with various reported beneficial health properties and a high smoke point. Also, the potential use of rice straw for the production of fuel and various other products has been reviewed by Abraham et al. (2016). Since rice husks are produced off-site during grain processing, a higher percentage is used, although it was also traditionally considered to be waste and often dumped and/or burned. However, rice husk is easily collected and cheap, so it has always had some use as an energy source for small applications, and in recent years a number of rice husk derived products have been developed, including polymeric composite resins and polymeric lumber as a substitute for natural wood, which are both produced

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<https://doi.org/10.1016/j.jobab.2020.07.001>

Available online 29 July 2020

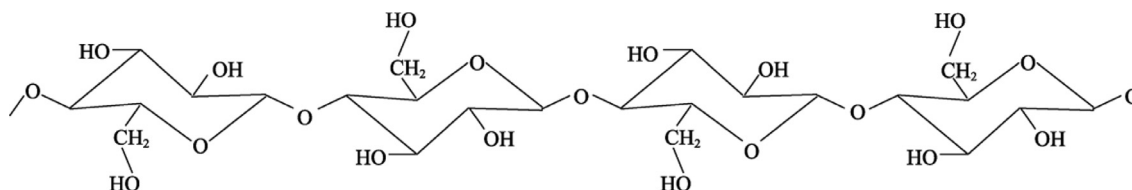
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Table 1

Major components of rice straw and husks (%).

	Cellulose	Hemicellulose	Lignin	Ash
Straw	32.0–38.6	19.7–35.7	13.5–22.3	10–17
Husk	28.6–43.3	22.0–29.7	19.2–24.4	17–20

Source: [Mirmohamadsadeghi and Karimi \(2020\)](#).**Fig. 1.** Representation of chemical structure of cellulose.

by combining ground rice husks and polymer resins, and solid pellets, which can be used in energy generation ([Defonseka, 2018](#)). The objectives of this review are to consider current practices for utilizing the waste straw and husks from rice production, and to present ideas for developing their full utilization, including the ash that remains from processes involving pyrolysis. Consideration is given to potential high value low volume products, such as silica and phenolic compounds, in addition to high volume lower value products, such as ethanol and methane. However, the extent to which many of these will be implemented will be determined by practical considerations, and the extent to which they are compatible with other factors that govern the functioning of societies.

1.2. Chemical composition and physical properties of rice straw and husk

Rice straw and husks contain a combination of cellulose, hemicellulose, and lignin, along with appreciable amounts of silica and other minor components, as summarized in [Table 1](#). Cellulose and hemicellulose are both polysaccharides; cellulose is a long straight-chain polymer containing exclusively β -glucose monomers ([Fig. 1](#)), whereas hemicellulose is a shorter cross-linked polymer that contains other sugars, such as xylose, galactose, mannose, rhamnose, and arabinose. In contrast, lignin is polymeric aromatic structures that involves oxidative coupling of 4-hydroxyphenylpropanoids, primarily *p*-coumaric, coniferyl and synapyl alcohols ([Fig. 2](#)) (e.g., [Ralph et al., 2004](#)). In cell walls, these polymers form very stable complex 3-dimensional structures known as lignocellulose, in which cellulose is surrounded by a monolayer of hemicellulose and embedded in a matrix of hemicellulose and lignin (e.g., [Fig. 3](#)).

Because of the stability of lignocellulosic materials, separation of the individual cell wall polymers is difficult, although there are various physical, chemical, and/or biological treatments that release the constituent sugars and phenols. Thermal decomposition products, such as chars and ashes, also have useful properties, although these are strongly influenced by the pyrolysis conditions and subsequent additional treatments. However, high value utilization of rice-derived biomass is still poorly developed ([Wi et al., 2013](#)), and field burning and soil accumulation of rice straw remain common practices, despite their contributions to environmental problems as a result of air pollution or ecosystem deterioration.

1.3. Activation and breakdown of cell wall polymeric structures

The first step in refining waste rice biomass involves breakdown of the bulk structure. Several technologies have been developed, which can broadly be categorized as biological, physical, chemical, or some combination of these, as illustrated in [Fig. 4](#). Generally, a pretreatment step removes lignin and/or hemicellulose, disrupts the cell wall structure, and increases the surface area and cellulose accessibility. Overall, biological pretreatment processes tend to be slow ([Hu et al., 2008a](#)), and some chemical and physical pretreatment methods are expensive ([Mosier, 2005](#); [Alvira et al., 2010](#)), whilst environmentally friendly pretreatments are often inefficient ([Li et al., 2009](#)). Thus an alternative approach to cellulose concentration is to produce plants with either lower lignin contents or lignin compositions that are amenable to chemical degradation ([Vanholme et al., 2010](#)).

1.3.1. Pretreatment methods

The silicified waxy surface protects rice straw, and needs to be damaged prior to attacking the lignocellulosic polymers. As illustrated in [Fig. 4](#), this can be achieved hydrothermally by steam treatment, which also alters the structural linkages between lignin and the carbohydrates ([Aski et al., 2019](#)), chemically by microwave-assisted pretreatment with FeCl_3 ([Lü and Zhou, 2011](#)), or dilute alkali, which removes lipophilic components ([Li et al., 2012](#)), or physically by superfine grinding ([Jin and Chen, 2006](#)) or high energy irradiation. Popping pretreatment increases the efficiency of subsequent cellulose-to-glucose conversion ([Wi et al., 2011, 2013](#)). However, the extent to which fiber components are separated and degraded is influenced by the experimental conditions ([Li et al., 2015a](#)), as illustrated for example by the production of a hydrolysate with high monomeric xylose content from rice straw pretreated with a combination of twin-screw extrusion and acid-catalyzed hot water extraction ([Chen et al., 2011a](#)).

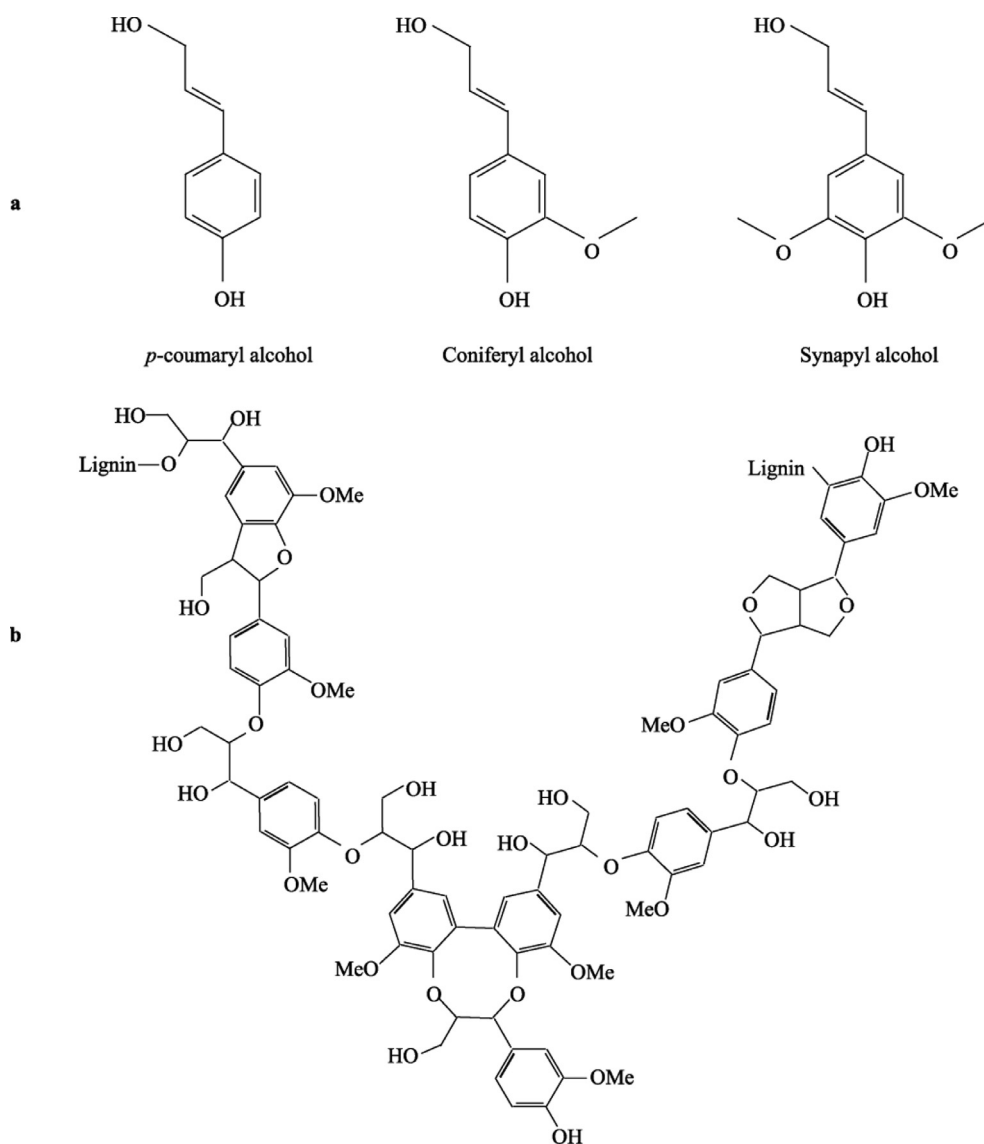


Fig. 2. Major building blocks of lignin (a) and a model structure for lignin (b).

Hemicellulose is easily hydrolyzed by dilute acid or alkali, but the beta acetal linkage in cellulose is more stable, and lignin resists many chemicals and microorganisms. In nature, lignin is only degraded by fungi of the *Basidiomycota* and *Ascomycota* families, although it is sensitive to strong alkali, and is selectively dissolved from rice straw by a deep eutectic solvent of choline chloride and urea (Pan et al., 2017). It can also be selectively removed from rice straw by aqueous ammonia, and subsequent treatment with dilute sulfuric acid removes most of hemicellulose and partially disrupts the cellulose structure (Kim et al., 2011). The use of ammonia-based pretreatments in lignocellulose biorefining has been reviewed by Zhao et al. (2020), who detailed the physicochemical mechanisms and performances of various methodological approaches with respect factors such as cell wall porosity, cellulose crystallinity, and lignin/hemicellulose structure. Additionally, Dagnino et al. (2013) have emphasized the importance of optimizing the concentration and heating time for acid pretreatment of rice husks results prior to enzymatic hydrolysis, and Park et al. (2010) have described the value of lime pretreatment for utilizing xylan, starch, and sucrose in addition to the cellulose in enzymatic saccharification and fermentation.

1.3.2. Lignin breakdown

Although it has traditionally been burned, lignin is an abundant source of aromatic compounds with potential to replace petroleum products in the production of many biobased materials. However, the depolymerization of lignin is complicated by its irregular structure and stability. One approach is to use Fenton reaction chemistry as an environmentally friendly treatment, which can operate under near-neutral conditions if an iron chelating agent such as citric acid is added (Sheng et al., 2017). Alternatively, hydroxyl

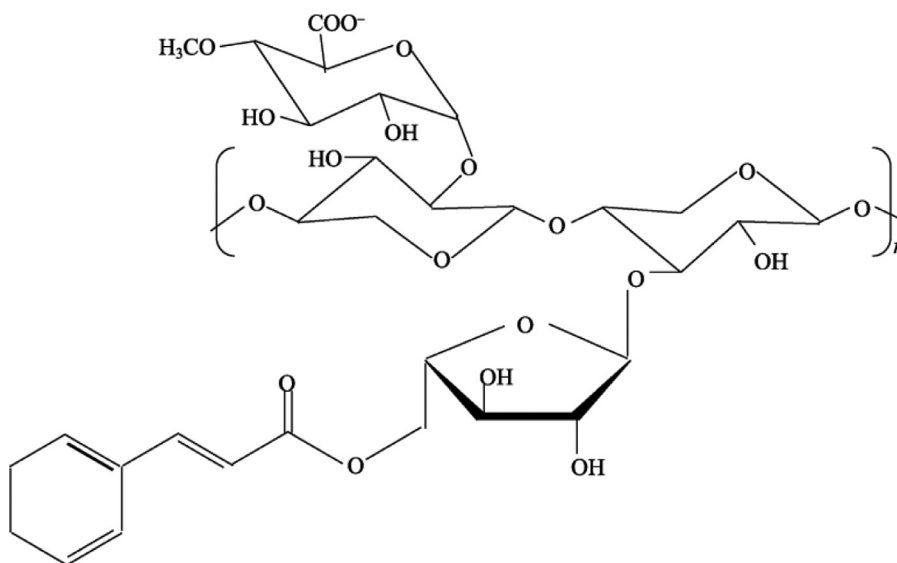


Fig. 3. Representation of linking of hemicellulose to cellulose and lignin.

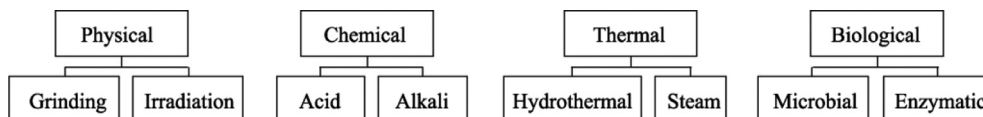


Fig. 4. Summary of main approaches used for breakdown of lignocellulosic materials.

radicals can be produced by decomposition of H_2O_2 by UV-radiation (Lu et al., 2014). However, the non-specificity of hydroxyl radical reactions results in the production of multiple compounds, although the main groups produced from rice husks are alkanes (from waxes), aldehydes and ketones (from cellulose and hemicellulose), and phthalates and arenes (from lignin). Recently, Gall et al. (2017) have described etherase enzymes that catalyze cleavage of ether bonds in lignin under conditions that recycle the cosubstrates NAD and glutathione. This promises to be a valuable new approach to be developed, although the depolymerization reactions in rice straw are strongly influenced by the lignin substructure (Lou et al., 2017). At the same time, biological engineering may produce lignin with greater homogeneity and specific functionality properties that simplify the separation of its breakdown products (Ragauskas et al., 2014).

A high degree of delignification, lignin recovery, cellulose enrichment and very high saccharification efficiency have been reported for alkali extracts of rice straw pretreated with an actinomycete isolate (Saritha et al., 2013), and a new lignolytic micromycete fungus *Myrothecium roridum* LG7 has also been shown to remove a large amount of lignin from pretreated rice straw. This could be recovered as a value-added product, and subsequent enzymatic hydrolysis released significantly higher amounts of reducing sugars than the untreated straw (Tiwari et al., 2013).

1.3.3. Fermentation processes

Fermentation is the metabolic process through which carbohydrates are converted to alcohols or acids:



Generally, yeasts convert sugars into alcohol, whereas bacteria convert carbohydrates into lactic acid. The *Trichoderma reesei* isolated from rotted rice straw residues produces cellulase, and effectively converts pretreated cellulose from rice straw into glucose, which yields ethanol on subsequent fermentation with yeasts, such as *S. cerevisiae* (Belal, 2013). Additionally, Zhang et al. (2016a) have reported that *Streptomyces griseorubens* produces cellulolytic enzymes that convert cellulose to reducing sugars, and that the hydrolyzed spent cells can be used as a nitrogen source for producing crude cellulase enzymes. These have high saccharification efficiency and show that the crude enzyme could be used as an alternative to commercial cellulase for saccharification. Also, addition of non-ionic surfactants and polyethylene glycol during enzymatic hydrolysis increases conversion of cellulose into fermentable sugars, and pretreatment of rice husks with various alkalis and acids produces cellulose and lignin with larger pore size and volume than untreated rice husk (Ang et al., 2013), which should be beneficial to fungal growth during fermentation.

1.3.4. Pyrolysis reactions

Biochar, hydrochar, and activated carbon are all pyrolysis products of agricultural biomass, and can be produced from both rice straw and husks. The various types of carbonization techniques that can be used to convert lignocellulosic biomass to carbon adsorbents have been reviewed by Chowdhury et al. (2013), who also addressed their applications for treating waste effluents, and subsequent regeneration. Biochars are formed by heating dry samples at moderate temperatures < 700 °C in the absence of O₂ (Lehmann, 2012), but their physical and chemical characteristics depend markedly on pyrolysis conditions. For example, Hu et al. (2008b) reported a gradual decrease in the intensities of OH, C–H and C–O groups in rice husk with increasing pyrolysis temperature, and a final char that was mainly of an aromatic polymer of carbon atoms. Also, the time, cost and energy consumption in biochar production can be decreased by using microwaves for heating (Huang et al., 2015).

Hydrochars are produced by hydrothermal treatment of undried samples at lower temperatures than biochars (Funke and Ziegler 2010; Kalderis et al., 2014). Although surface areas porous structures are only developed at temperatures > 300 °C, low temperature hydrochars have potential value as fuel.

Activated carbon is essentially a biochar that is activated either by hot steam or various types of chemical (acid, alkali, etc.). Its properties vary appreciably with production conditions; for example Wang et al. (2011b) have reported that with rice husks carbon contents increase with increasing temperature (in the range of 400–800 °C) along with increases in specific surface area and pore volume, whilst the number of surface O–, C–H, C=O, and C=C surface groups decrease. Also, by using ortho-phosphoric acid in the activation process, highly mesoporous activated carbons have been obtained from rice straw at temperatures of 350–500 °C (Fierro et al., 2010). The porous carbon derived from rice husks by a combined chemical/thermal process has been reported by Chen et al. (2011c) to have fast kinetics and appreciable adsorption capacities that make it suitable for new applications such as catalytic supports, battery electrodes, capacitors, and gas storage.

Cellulose and lignin are both destroyed by burning, and at 500–700 °C amorphous silica is the main product from both rice straw and husk. Under optimum combustion conditions, ashes contain ~90% of amorphous silica with microporous structures and high specific surface areas (Chindaprasirt et al., 2007). However, the relative amounts of amorphous and crystalline forms of silica are determined by the temperature and duration of burning, and uncontrolled combustion at temperature > 700–800 °C produces significant amounts of cristobalite and tridymite, which are unreactive. Many applications of ashes require specific properties, such as reactivity for cement and concrete, chemical purity for synthesizing advanced materials, whiteness and appropriate particle size for filler applications, and high surface area and porosity for use as an adsorbent and catalyst (Chandrasekhar and Pramada, 2006), and there is a need to integrate the production conditions for ashes with requirements for their proposed uses.

2. Agricultural uses

2.1. Soil treatments

Traditionally, much of the produced rice straw has been burned in the field, as a quick and easy method of disposal. However, this results in the generation of atmospheric pollution from smoke and greenhouse gases; the latter are affected by moisture which enhances emission of CO, CH₄ and other organic carbons, whilst inhibiting N₂O emission (Arai et al., 2015). Some incorporation of straw into the soil is a common management practice for improving fertility (Liu et al., 2014a), and to counter the detrimental effects of prolonged agricultural activity (Ray et al., 2012), but its effect on increasing methane emission is a concern (Conrad, 2007), although it has been reported recently that such emissions may have been overestimated (Jiang et al., 2019).

Soil properties can be improved by amending with biochars prepared from either rice straw or husks; these increase the pH, CEC and nutrient availability (Cui et al., 2011; Liu et al., 2014b; Li et al., 2019), and decrease nitrate leaching (Ghorbani et al., 2019). Biochar amendment has also been reported to decrease Pb(II) availability and accumulation in rice (Jiang et al., 2012; Li et al., 2016), and to have a synergistic effect with Si-induced liming in inhibiting Cd uptake from a Cd-contaminated soil (Sui et al., 2020). Furthermore, significant increases in rice shoot Si contents have been observed after biochar amendment, and increased rice yields have been reported in soils with low silica content after application of xerogel silica prepared from micronized rice husk ash (Rambo et al., 2011). However, the value of biochar as a soil amendment to improve soil properties is strongly influenced by soil type.

2.2. Animal husbandry

Although straw is traditionally used as bedding for livestock, it has only limited value for use as feed. All vertebrates lack enzymes to break β -acetal links, and ruminant animals rely on symbiotic bacteria to break down cellulose in the gastrointestinal tract. Moreover, dry rice straw has limited digestibility, although this can be improved by pretreatment with ammonia or urea (van Soest, 2006), and poor nutritional value because of its low protein content and high levels of lignin and silica. Therefore, it is common to convert it to silage to improve nutrient availability. Developments in rice straw harvesting technology for silage production have been considered by Wang et al. (2011a), and various practical aspects of silage processing have been reviewed by Oladosu et al. (2016). These include the use of various types of additive to improve the fermentation quality, including supplementation with yeasts, such as *Candida tropicalis* (Wang et al., 2016b). In addition, Gunun et al. (2013) reported that treatment of rice straw with urea improves feed intake, digestibility, rumen fermentation and efficiency of microbial N synthesis.

2.3. Medium for mushroom production

Several types of mushroom are able to break down lignocellulosic materials, and their cultivation represents an economical and environmentally-friendly approach to the utilization of agricultural wastes. Kamthan and Tiwari (2017) list *Agaricus*, *Pleurotus*, *Lentinula edodes*, *Volvallella volvacea*, and *Ganoderma* as five common mushroom species that are suitable for cultivation on agricultural wastes, though it is only *Pleurotus* that is currently grown to any appreciable extent on rice straw. Addition of cotton seed husk increased its yield and physical properties, whilst addition of rice husk improved the performance and nutrient content of *Pleurotus* grown on composted sawdust (Yang et al., 2013).

3. Energy generation

As with other organic wastes, rice straw can be used for energy generation, including ethanol, biogas, and bio-oil, as well as direct burning. Although ethanol is the most widely used biofuel for transportation, its production from lignocellulose materials is still poorly developed (Balat, 2011). However, rice straw is the most abundant renewable lignocellulose resource (Kim and Dale, 2004), although its use for bioethanol production is limited by its high silica and lignin contents, which inhibit fermentation. Thus lignin must be first removed before the carbohydrates can be hydrolyzed for biofuel production, and various physical and chemical methods are described in Section 1.3 as pretreatments that enable production of fermentable sugars by biocatalysts. Since biological catalysts often function synergistically (Bajaj and Mahajan, 2019), selection of an appropriate pretreatment procedure is a major challenge for developing wide scale commercial bioethanol production from rice straw (Binod et al., 2010), and the pretreatment method, choice of yeast, and fermentation conditions all need to be considered.

3.1. Direct use as a fuel

Although pyrolysis and gasification can be used to produce bio-diesel, rice husk pellets also represent an alternative to diesel oil and coal for small scale electrical power generation (Quispe et al., 2017). The high production of ash rich in silica and alkali can result in agglomeration and damage to combustion equipment. Nevertheless, there are potentially valuable uses of the ash, as described in later sections of this review. Rice husk briquettes formed using starch or gum Arabic as binders have superior combustion properties to firewood (Yahaya and Ibrahim, 2012), and a reactor using rice husk supplemented with sawdust or charcoal to produce high quality fuel has been described by Wu et al. (2015). Carbonization of rice husk produces char with moderately high heating value (Maiti et al., 2006) with starch as a binder and ferrous sulfate or sodium hypophosphite added to improve ignitability.

3.2. Alcohol production

3.2.1. Pretreatments

Chemical pretreatments for glucose production are described in Section 1.3.1. These may be based on alkali, acid, or ammonia, but alkali-based treatments tend to be the most effective, because of their ability to break the ester bonds between lignin, hemicellulose, and cellulose (Rahnama et al., 2013). Also, alkali produces less furfural, 5-HMF, and vanillin than acid pretreatments, and generally improves cellulose fiber swelling. Large improvements in enzymatic hydrolysis were obtained by pretreating rice straw with *N*-methyl morpholine *N*-oxide or 1-buthyl-3-methylimidazolium acetate at 120 °C, which reduced cellulose crystallinity, and resulted in complete or near complete conversion of glucan glucose on enzymatic hydrolysis (Poornejad et al., 2013). Physical treatments that have been used for rice straw pretreatment include steam explosion (Zhou et al., 2016; Aski et al., 2019), grinding and milling (Jin and Chen, 2006).

3.2.2. Ethanol production

After appropriate pretreatment, cellulose and hemicellulose are hydrolyzed rapidly to monosaccharides by cellulase and then fermented to ethanol. An example of the conditions used for enzymatic hydrolysis of rice straw is described by Khaleghian et al. (2017) who used a mixture of cellulase and β -glucosidase in the presence of sodium azide at 45 °C in 0.05 mol/L sodium citrate buffer (pH 4.8) containing 5% (w/V) solid. Fermentation of rice straw without nutrient supplementation has been described by Priya et al. (2016) using the yeast *Saccharomyces cerevisiae* after pretreatment with the fungus *Myrothecium roridum*, although production of aromatic compounds limited the fermentation efficiency. Also, oligomeric sugars in the liquid fraction of hot water-pretreated rice straw are more amenable to membrane filtration than monomeric sugars, and the low molecular weight fermentation inhibitors, acetic and formic acids, are decreased appreciably by the xylose-fermenting recombinant *S. cerevisiae* (Sasaki et al., 2014).

Various methods to improve ethanol production efficiency have been described, including simultaneous saccharification and fermentation with an optimized enzyme cocktail and the xylose-fermenting fungus *Mucor circinelloides* (Takano and Hoshino, 2018). Combining fermentation with biological pretreatments can also improve the efficiency of ethanol production, as shown by the *in situ* hydrolysis of rice straw with a mixed culture of *Trichoderma reesei* and *T. viride*, which excrete lignin-degrading enzymes and cellulose, and fermentation with *S. cerevisiae* and *Candida tropicalis* co-immobilized in polymer beads composed of sodium alginate, polyvinyl alcohol, and silicon dioxide which protect the yeasts (Wu et al., 2016a). Also, Sarabana et al. (2018) have recently described a consolidated bioprocess in which rice straw is first pretreated with alkaline hypochlorite to facilitate cellulase production by *Trichoderma reesei*, and then fermented with a culture of *S. cerevisiae* and *Aspergillus oryzae*. The economics of bioethanol production can also be improved by co-producing high value products in integrated processes, an example being extraction of the flavonoids

sapigenin and kaempferol from rice straw (Ma et al., 2019). Additionally, the by-product of bioethanol production from rice straw known as black liquor is rich in lignin and silica. These can be recovered by hydrolysis with dilute acid followed by alkaline peroxide delignification, and high quality products then isolated separately by sequentially decreasing the pH with dilute sulphuric acid (Minu et al., 2012).

3.2.3. Butanol production

A combination of acetone, butanol, and ethanol is produced from rice straw by ethanol organosolv pretreatment, enzymatic hydrolysis, and fermentation by *Clostridium acetobutylicum* (Amiri et al., 2014), and near complete utilization of soluble sugars has been reported in a bioreactor (Ranjan et al., 2013). Generation of butanol has also been reported from a co-culture of cellulolytic *Clostridium thermocellum* and butanol-producing *C. saccharoperbutylacetonicum* and delignified rice straw pretreated with NaOH (Kiyoshi et al., 2015); and addition of cellulase enhanced exoglucanase activity on lignocellulose degradation, and significantly increased butanol production. Furthermore, Chen et al. (2013a) have shown that a high initial cell concentration of *C. saccharoperbutylacetonicum* minimizes interference from other microorganisms and gives biobutanol production in non-sterile conditions that is comparable to a sterile system.

3.3. Biogas production

Biogas can be generated by anaerobic microbial degradation of a combination of treated rice straw and animal waste. However, the initial straw treatment is a critical step in biogas production, and care in optimizing its pretreatment is of considerable value. Mechanical crushing increases the surface area (Kratky and Jirout, 2011), and extrusion expands of the fibril structure (Chen et al., 2014), whilst $\text{Ca}(\text{OH})_2$ pretreatment enhances enzyme hydrolysis of extruded rice straw by effectively removing lignin (Gu et al., 2015). The lignin content is also reduced by steam explosion (Aski et al., 2019), whereas ultrasound pretreatment reduces the hemicellulose content and also increases biogas production from rice straw (Pansripong et al., 2019). Methane is also produced from the residue remaining after removing carbohydrates by wet explosion pretreatment and enzymatic hydrolysis to make the lignin accessible for anaerobic digestion, although a second wet explosion treatment involving NaOH was required to optimize methane generation (Usman Khan and Kiaer Ahring, 2020).

Rice husk briquettes or pellets are produced by compression with small quantities of additives for adhesion to improve their combustion performance and can be used as a substitute for fossil fuel in the gasification process to convert rice husk synthesis gas in a reactor with a controlled amount of air; this gas can then be used as fuel or in a cogeneration system to produce electricity.

3.4. Bio-oil production

Biomass is a unique resource for sustainable production of bio-derived chemicals and fuels to replace fossil fuel products. Although lignin is a major component of lignocellulose materials its complex cross-linking polymeric network makes it recalcitrant for current chemical technologies, and various catalysts are being developed for its depolymerisation (Pineda and Lee, 2016). In this respect, Ni-doped catalysts have been described recently by Du et al. (2020) as facilitating cleavage of the β -O-4 aryl ether bond and producing bio-oil, liquid fuels, and aromatic chemicals from rice husk lignin. However, the catalytic reaction is temperature-, time-, and solvent-dependent, and needs to be optimized for biorefinery development.

Fluidised bed fast pyrolysis with catalytic treatment of rice husk can economically produce primary pyrolysis oil that is suitable as boiler fuel oil and for the production of catalytically treated, upgraded, liquid-products (Islam and Ani, 2000). Phenolic compounds are the dominant product along with some furans and benzenediols (Karagoz et al., 2005). The majority of oxygenated hydrocarbons are distributed at n -C₁₁, and the major gaseous product is carbon dioxide, along with carbon monoxide, methane, ethylene, ethane and propane. Fast pyrolysis of rice husk in the range of 400–600 °C gives a high yield of bio-oil, and Alvarez et al. (2014b) have described a bench-scale plant that allows continual removal of char, which can be upgraded to produce amorphous silica and activated carbon. Bio-oil yield decreased slightly with increased temperature, but gas production was very low in the whole range of temperature studied.

4. Production of adsorbents for environmental control

In the development of sustainability, utilization of one waste material to control pollution caused by another is of high significance for amelioration of environmental problems. In this respect, both rice straw and husks have been used as environmental adsorbents in their natural forms and after various types of treatment to improve their sorption capacities. Examples of such uses are presented in this section.

4.1. Untreated rice straw and husk as adsorbents

There are several reviews which demonstrate the ability of rice husks to remove various pollutants from water, including dyes, phenols, organic compounds, pesticides, inorganic anions, and heavy metals (Ahmaruzzaman and Gupta, 2011; Noor Syuhadah and Rohasliney, 2012; Shamsollahi and Partovinia, 2019). Specific examples include the removal of the dyes Direct Red-31 and Direct Orange-26 (Safa and Bhatti, 2011) and Congo Red (Han et al., 2008), and the heavy metals lead (Zulkali et al., 2006), antimony (Khalid et al., 2000), and thallium (Alalwan et al., 2018). Rice husk can also be used as solar absorber plates in the distillation process for

desalinating sea water (Syarif et al., 2015; Ummah et al., 2015). There are also many publications which describe the potential use of rice straw as a cheap adsorbent for the removal of heavy metals from contaminated waters (e.g., Buasri et al., 2012), whilst the spent straw could have value as a bio-ore. The adsorption capacity varies with both metal ion and water pH (Rocha et al., 2009; Nawar et al., 2013), and is thus strongly influenced by the metal speciation as well as the composition of the straw surface. However, most heavy metal ions show maximum adsorption near pH 5, whereas Cr adsorption is favored by strongly acidic conditions (Gao et al., 2008), and may be the consequence of reduction of Cr(VI) to Cr(III) at low pH. For practical purposes, an artificial intelligence network has been described for predicting with high accuracy cadmium adsorption on rice straw (Nasr et al., 2017), and a similar approach could be developed for other metal ions. As with rice husk, straw can be used as an adsorbent for other water pollutants, including phenolic compounds, which can be recovered with alkali (Amin et al., 2012), and anionic species in general.

4.2. Chemical and biological modification of straw and husk

Despite the extensive use of rice straw and husks described in the previous section, a wide range of treatments have also been proposed/developed for their improvement as adsorbents (e.g., Daffalla et al., 2010; Noor Syuhadah and Rohasliney, 2012). Several examples are presented in this section to give an overall view of the range of treatments and the scope of their applications for removal from water of cations, anions, and uncharged molecules.

The adsorbent surface of rice straw is dominated by methyl/methylene, hydroxyl, quaternary ammonium, ether and carbonyl groups, and adsorption capacity is increased by increasing the number of quaternary ammonium groups (Cao et al., 2016) or the introduction of carboxyl groups, as seen with copper, lead (Wong et al., 2003), and chromium (Gao et al., 2008), although unsurprisingly, sorption capacities are reduced by the presence in solution of competitive cations and chelators (Bishnoi et al., 2004). Modification of rice husk with H_3PO_4 increases its adsorption of copper (Zhang et al., 2014), nickel and cadmium (Ajmal et al., 2003), and a system for continuous removal of Ni(II) from aqueous solution has been described by Azadi et al. (2018). Furthermore, cellulose phosphate prepared from NaOH-pretreated rice straw by reaction with phosphoric acid in the presence of urea has high heavy metal adsorption capacity that is enhanced by the use of microwave heating during its preparation (Rungrodnimitchai, 2010, 2014). Furthermore, spontaneous and endothermic adsorption was observed for chromium and nickel on rice straw functionalized with amine groups (Wu et al., 2016b). A Fe_3O_4 /steam-exploded rice straw composite with polyethyleneimine via glutaraldehyde crosslinking that can be easily separated by a magnetic field has been described by Zhang et al. (2018c) as having a high capacity for the removal of Cr(VI) from wastewater; maximum adsorption was observed at pH 2.0, and involved partial reduction to Cr(III). Also an adsorbent formed by grafting mercaptan functional groups onto rice straw was shown to be effective for removing mercury from water by a spontaneous and endothermic mechanism (Song et al., 2013, 2016). Rice straw-based hydrogels also show high capacity for removing heavy metals from wastewaters (Basta et al., 2013). An alternative use of the high adsorption capacity of modified rice husks for heavy metals has been proposed by Teixeira Tarley et al. (2004) for an on-line preconcentration system for their determination by flame atomic absorption spectrometry.

Rice straw derived adsorbents that involve chelation to the N of primary amine and the O of alcoholic hydroxyl groups in addition to ion exchange have also been developed for the concentration of precious metals. Examples include selective adsorption of PdCl_4^{2-} on modified rice straw (Zhang et al., 2017), and AuCl_4^- on chemically modified lignin derived from rice straw (Zhang et al., 2018a). This latter adsorbent operated by an initial ion exchange process, followed by reduction of the gold to Au(0) in HCl by the phenolic groups. Modified lignin also has a high adsorption capacity for PtCl_6^{2-} , which involves reduction of Pt(IV) to Pt(II) by hydroxy groups followed by coordination of PtCl_4^{2-} to amine groups (Zhang et al., 2018b).

Several adsorbents derived from rice straw and husks have also been developed for removal of dyes from wastewaters. Examples of use with cationic dyes include rice straw modified with citric acid, which increases the specific surface area and pore size, and was used for adsorption from aqueous solution of Crystal Violet (Chakraborty et al., 2013), or Methylene Blue (Fathy et al., 2013). Adsorption of Methylene Blue was also used to demonstrate the ability of lignocellulosic residues from enzymatically hydrolyzed rice straw pretreated with FeCl_3 to adsorb cationic dyes (Kim et al., 2014). Similar examples have been reported for chemical treatments of rice husks for adsorption of cationic dyes, as illustrated by Methylene Blue (Papita, 2010), and Malachite Green (Chowdhury et al., 2011). Organosolv lignin, which is a byproduct of delignification of steam-exploded rice straw with high contents of phenolic and aliphatic hydroxyl groups also has good adsorption of Methylene Blue in the pH range of 5–9 (Zhang et al., 2016b).

Rice straw can also be modified to have anion exchange capacity, as seen by its strong sulfate adsorption capacity after introducing epoxy and amino groups through reaction with epichlorohydrin and trimethylamine (Cao et al., 2011). Adsorption of acid dyes can be achieved by grafting rice straw with dimethylaminoethyl methacrylate (Mostafa et al., 2012), and nanoparticles formed by crosslinking modified rice husk with poly(methylmethacrylate-co-maleic anhydride) have been developed as novel adsorbents for both heavy metal ions (e.g., Pb(II)) and dyes (e.g., Crystal Violet) (Masoumi et al., 2016). Novel green ceramic hollow fiber membranes derived from rice husk ash have been shown to act as both an environmentally friendly adsorbent and separator for efficient heavy metal removal from water (Hubadillah et al., 2017), and a novel amphoteric adsorbent that can efficiently remove both cationic (Methylene Blue) and anionic (Qacid Green 25) dyes from aqueous solutions has been produced by incorporation of quaternary ammonium and carboxymethyl groups (Zhang et al., 2012).

A hydrophobic adsorbent prepared from rice straw by acetylation with acetic anhydride in the presence of 4-dimethylaminopyridine catalyst has potential for use in oil cleanup (Sun and Sun, 2002), and an alternative rice straw-derived adsorbent for clean-up of oil spills has been produced by filling rice straw in a porous polyurethane matrix (Hoang et al., 2018).

Microbially-treated rice straw also has potential for development as biosorbents. Examples include the product from fermentation with *Aspergillus niger* for rapid removal of Cu(II) from aqueous solutions at pH 4.0–6.0 (Wang et al., 2016a), and the removal of

Methylene Blue from wastewater by a combination of rice straw powder and the white rot fungus *P. chrysosporium* (Cheng et al., 2015). In both examples, the improved adsorption capacity compared to raw rice straw was attributed to the introduction of functional groups with chelating ability on the straw surface.

4.3. Biochars and activated carbons

The influences of physical and chemical conditions on the properties of activated carbons prepared from various agricultural residues have been reviewed by Ioannidou and Zabaniotou (2007), who also compared their characteristics with commercial activated carbons and products from other sources. Depending on the process conditions, activated carbons could be produced with BET surface areas of 250–2410 m²/g and pore volumes of 0.022–91.4 cm³/g.

4.3.1. Biochars and hydrochars

Various treatments are used to increase the porosity and adsorption capacity of biochars and hydrochars for different types of adsorbate, and this section presents examples to illustrate the scope of their applications. The time and cost of biochar production can be minimized by using microwaves for heating, and Huang et al. (2015) report that such products have greater CO₂ adsorption capacity than biochar produced by conventional pyrolysis. Pretreating rice husk with H₂SO₄ and NaOH before heating results in a product with increased phenol adsorption capacity (Al-Sultani and Al-Seroury, 2012), and rice husk biochar activated by a 1-step KOH-catalyzed pyrolysis under CO₂ has higher surface area and better phenol adsorption than conventional activated biochar (Shen and Fu, 2018). Furthermore, orthophosphate-treated biochars represent inexpensive and effective adsorbents for a variety of applications, as illustrated by the improved adsorption capacity for the pesticides, atrazine and imidacloprid by phosphoric acid treated rice straw biochar (Mandal et al., 2017).

A rice husk derived biochar with specific silanol groups and oxygen functional groups produced by heating to 300 °C is an effective adsorbent for the gold-thiourea complex (Nakbanpote et al., 2000), and elution of the adsorbed gold with sodium thiosulfate was aided by the lower level of thiourea adsorption compared with activated carbon. Such biochars are highly selective for Au(III) and inert to Pt(IV), Pd(II) and other base metals (Chand et al., 2009), and represent potential alternatives to commercial activated carbon for gold concentration.

Combining different agricultural wastes may produce biochars with enhanced sorption properties, as shown by the presence of adsorption sites from phenolic and carboxyl groups along with amorphous silica in biochars from rice straw/cattle manure mixtures (Qian and Chen, 2013). It is also possible to design hydrochar composites with specific sorption properties, as illustrated by the high adsorption of phosphorus on the char synthesized by hydrothermal carbonization of lanthanum pretreated rice straw in the presence of competing anions (Dai et al., 2014); there was a synergistic effect between the La and the hydrochar, and the composite has potential for use in phosphorus removal/recovery from wastewater.

4.3.2. Activated carbon

Early literature on the use of activated carbon from rice husk for removing heavy metals and dyes from water was reviewed by Chuah et al. (2005), and the present section simply presents a few more recent examples. Activated carbons are effective for removal from water of heavy metal ions, such as Cr(VI) at low pH (Hsu et al., 2009), Cu(II) and Pb(II) (Nono and Abdel-Sabour, 2015), phenol (Sarker and Fakhruddin, 2017), chlorophenols (Wang et al., 2007), basic dyes (Hameed and El-Khaiary, 2008), and acidic dyes (El-Bindary et al., 2014, 2015). In addition, activated carbon prepared from rice straw by carbonization and KOH activation has high adsorption capacity for aqueous solutions of bisphenol A (Chang et al., 2012), and the pesticide, carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) (Chang et al., 2014), whilst activated carbon modified by KMnO₄ oxidation can remove fluoride from natural waters (Daifullah et al., 2007). Furthermore, burnt rice straw compares favorably with other adsorbents currently used for the removal of As(III) from ground water (Faruque and Uddin, 2012). However, there are still continued efforts aimed at developing methods for improved performance for specific pollution problems.

Activated carbon from rice straw treated with a combination of (NH₄)₂HPO₄ and preoxidation at 200 °C prior to activation at 700 °C has good adsorption capacity for Methylene Blue (Gao et al., 2011). Furthermore, treating rice straw carbon with H₃PO₄ at 350–500 °C produces a highly mesoporous structure (Fierro et al., 2010). This can be further improved by pre-carbonisation at 400 °C prior to activation with potassium hydroxide at 700 °C, and the product has strong anion and cation adsorption capacity, as demonstrated by the dyes Congo Red and Methylene Blue (Sangon et al., 2018). Adsorption of Malachite Green from aqueous solution by rice husks modified by H₃PO₄ or NaOH followed by carbonization in N₂ at 500 °C occurs on carbon-rich rather than on silica rich-sites with capacity similar to that of commercial activated carbon (Rahman et al., 2005). Similar dye adsorption behavior for activated carbon from rice husks has been reported for Safranin-T (Gupta et al., 2006) and Methylene Blue (Lin et al., 2013). Activated carbon prepared from rice husks can also be used to remove natural organic matter from water. The factors that affect its performance have been reviewed by Menyá et al. (2018), who showed that it could be as effective as commercial activated carbon.

The combined presence of organic compounds and heavy metal ions in water can either enhance or suppress their adsorption. For example, in the simultaneous removal of Cd and sulfamethoxazole by rice straw biochar from co-contaminated water, Han et al. (2013) observed much higher adsorption of sulfamethoxazole in the binary system than for the antibiotic alone, whereas Cd was similar in both systems. This result is probably of the consequence of the Cd complexes with carboxyl or hydroxyl groups formed on the surface of the biochar acting as sites for sulfamethoxazole adsorption. However, the opposite effect was observed with adsorption of U(VI) on activated carbon, where the presence of humic acid suppressed adsorption by holding the U in solution, and thus needs to be removed from wastewater before extraction of U (Yakout et al., 2013). Care should also be exercised in interpreting results, as

demonstrated by Kumagai et al. (2007), who showed that residual fluid components in carbonized rice husks may be more important than their porosity for oil spill cleanup.

The preparation of porous carbons for CO₂ capture at low pressures by KOH activation of rice husk char has been described by Li et al. (2015b). High CO₂ uptake ability and CO₂-over-N₂ selectivity is favored by low activation temperature and small KOH/char ratio, and is considered to result from the presence of micropores with a narrow size distribution.

4.4. Ashes

The solid products of rice husk combustion are dominated by silica, and have applications in pollution control and environmental preservation (Foo and Hameed, 2009). Rice husk ash is a good adsorbent for heavy metals, such as lead and mercury (Feng et al., 2004; Naiya et al., 2009), with adsorption being favored by small particle size, high solution pH, and low supporting electrolyte concentration. Also, rice husk ash with surface modified by aluminum hydroxide has excellent fluoride adsorption capacity (Ganvir and Das, 2011).

Rice husk ash has been used for the efficient removal of phenol from aqueous solutions (Kermani et al., 2006), and for the adsorption of various dyes, such as Methylene Blue, Congo Red and Indigo Carmine (Simonov et al., 2003; Chandrasekhar and Pramada, 2006; Chowdhury et al., 2009; Lakshmi et al., 2009; Sarkar and Bandyopadhyay, 2010), where the maximum adsorption from aqueous solutions can be even higher than with activated carbon from rice husk (Chandrasekhar and Pramada, 2006).

Rice husk ash is also an excellent adsorbent for removing impurities from biodiesel as a result of its high silica content and the presence of meso and macropores (Manique et al., 2012), and production of high quality mesoporous white silica from combustion of the residual biomass from ultrasound-sulfuric acid treatment of rice straw could help improve the economics of bioethanol production (Rehman et al., 2013). More recently, various methods for producing silica and silica aerogel from rice husk ash have been reviewed by Zou and Yang (2019), along with the factors that influence their physical and chemical properties. Additionally, the problem of disposal of black liquor can be resolved by developing adsorbents from black rice husk ash that have been shown to be effective in removing Cr(VI) from aqueous solutions (Georgieva et al., 2015).

5. Construction materials

Various applications of rice husk ash for products used in the construction industry have been reviewed by Singh (2018); these include fillers, additives, abrasive agent, oil adsorbent, and suspension agent for porcelain enamels along with use as a pozzolan and for partial replacement of cement. However, each application requires specific properties, and the suitability of ashes for any particular use is influenced by the production conditions.

5.1. Building products

Natural fibers from agricultural wastes can be utilized for the production of light weight and low cost polymers for applications in building and construction. The cost of cement bricks with good thermal insulation properties, adequate mechanical properties and fire resistance can be reduced by incorporating rice straw (Allam and Garas, 2010; Elkady et al., 2011), and rice straw derived composites using starch based adhesives have potential for use as ceiling panels and bulletin boards (Liu et al., 2012); for these, corn starch produced composites with better flexural properties than those with cassava or potato starch, and hot-water treatment of straw gave better interface and higher flexural properties than alkali treatment. After appropriate pretreatment, rice straw can also be used for fibreboard manufacture (Theng et al., 2017, 2019). Twin-screw extrusion uses much less energy than steam digestion plus defibration in producing the pulp for fiberboard, and produces a good compromise between density and flexural properties.

By partially removing hemicellulose and lignin by mechanical-high pressure steam treatment of rice straw, cellulose crystallinity is improved and the degradation temperature increased to > 280 °C, thus making it suitable for use in reinforced-polymer composites (Chen et al., 2011b). Also, the use of rice husk as a filler in composite materials has been reviewed by Arjmandi et al. (2015), who point out that composite properties are strongly influenced by fiber-polymer interactions, and that improved understanding is still needed on the mechanisms of interaction between the polymers and fillers. In an investigation of the bonding between rice straw fibers and eco-urea formaldehyde, Basta et al. (2014) showed that the mean hydrogen bond strength is more closely related to the efficiency of removing silica than the wax.

5.2. Use of ashes as pozzolans

An important use of rice husk ash is as a pozzolan, which is a finely divided material that in the presence of water reacts with calcium hydroxide released by hydration of Portland cement to form calcium silicate hydrate and other cementitious compounds. Various uses of rice husk ash as a pozzolan and a component of cement have been reviewed by Khan et al. (2015) and Singh Aulakh et al. (2018). Burning rice husk below the silica crystallization temperature produces an ash that is predominantly amorphous in character (Chindaprasirt et al., 2007; Ramezaniannpour et al., 2009) with its reactivity derived primarily from the internal surface of microporous particles. Quickly cooled ash has the maximum number of silanol groups that are important for a pozzolanic cement additive (Nair et al., 2008), and pozzolanic activity is increased by grinding (Rukzon et al., 2009). Concrete setting increases with increased ash content, and when used in masonry concrete, rice husk ash imparts good strength and durability (Zareei et al., 2017). Furthermore, addition of 20–30% rice husk ash increases resistance to sulfate, acid, and chloride attack (Chindaprasirt, et al., 2007,

2008), whilst 20% of Portland cement can be replaced by rice husk ash without adversely affecting its strength (Habeeb and Mahmud, 2010). Additionally, the water demand by rice husk ash when used as a partial replacement for cement can be controlled by mixing with clinker during cement manufacture or by blending it with cement at the point of use. The rice husk ash fixes free lime released during hydration of clinker silicates, and the amorphous silica reacts with $\text{Ca}(\text{OH})_2$ in the secondary hydration reaction to form a porous structure with large specific surface area that enhances the strength and durability of the concrete.

As a result of its high contents of silica, alkaline and alkaline earth metals, rice straw ash can replace feldspar and quartz in the production of ceramic materials (Guzmán et al., 2015b), and can also form part of an alternative raw material for producing porcelain tiles by replacing non-plastic components, which together with clays constitute the major constituents of porcelain tiles (Guzmán et al., 2015a).

6. Other products

6.1. Silica

In addition to its roles in uses of rice straw and husks described in the preceding sections, pure silica can also be produced from these materials. Silica along with sugar has been produced from rice straw by ultrasound-sulfuric acid treatment followed by a short thermal treatment (Rehman et al., 2013), and silica can be recovered from rice husk char by extraction with Na_2CO_3 (Alvarez et al., 2014a), or precipitation with CO_2 from the hot alkali extract of rice husk ash that had been leached with acid (An et al., 2011).

6.1.1. Catalyst production

The high silica content of rice husk makes it a valuable material for catalyst production, and Li_2SiO_3 prepared by calcining ground rice husk ash with Li_2CO_3 at 900 °C in air has been used for transesterification of soybean oil with methanol at atmospheric pressure to give near 100% conversion to biodiesel (Chen et al., 2013b). Biodiesel has also been produced from waste cooking oil using a heterogeneous catalyst prepared by sulfonating pyrolyzed rice husk with concentrated sulfuric acid (Li et al., 2014). Additionally, a rice husk-based silica supported iron catalyst that can efficiently remove and degrade the xanthene dye Rhodamine B by a Fenton-like process has been described by Gan and Li (2013), and its ability to degrade the dye could be enhanced by salts such as Na_2SO_4 and NaCl in wastewater from the textile industry.

6.2. Separation and uses of cellulose derived from rice waste

6.2.1. Extraction and purification of celluloses

Rice straw fibers are considered to have better properties than other natural cellulose fibers obtained from agricultural byproducts (Reddy and Yang, 2006), and are suitable for most high-quality fiber applications, including the production of textiles, composites, and as substitute for other natural and synthetic fibers in various applications. Cellulose fibers can be extracted from rice straw or husk by alkali and bleaching treatments (see Section 1.3.1), and recently Gou et al. (2018) have described an instant catapult steam explosion technique which converted rice straw into cellulosic fibers with good accessibility, and at the same time protected them from being over-hydrolyzed. Increased cellulose crystallinity and overall cellulose content can be obtained with combined microwave-alkali-acid pre-treatment of rice straw (Akhtar et al., 2017), whilst reducing the hemicelluloses and lignin by almost 50% in the solid fraction of the biomass.

6.2.2. Nanocellulose

Because of its high strength and low toxicity, micro- and nano-crystalline cellulose have potential uses in a number of biological applications, including use as a filler in foods and pharmaceuticals, enzyme immobilization, antimicrobial and medical materials. Various applications of nanocrystalline cellulose have been reviewed by Lam et al. (2012), who focused specifically on modifications with chemical functional groups or inorganic nanoparticles.

Various methods are used for preparing nanocellulose, the simplest being sulphuric acid hydrolysis of alkali treated rice straw or husk (Johar et al., 2012; Lu and Hsieh, 2012); freeze-drying nanocellulose suspensions produces long ultra-fine fibers with non-porous or macroporous structures. Nanocellulose films have been prepared by TEMPO-mediated oxidation and mechanical defibrillation of dewaxed and alkali treated suspensions of rice straw powder. At the same time, hemicelluloses/lignin composites can be isolated from the aqueous suspension, and solutions containing mixtures of these fractions cast into films with good flexibility, transparencies, mechanical and moisture barrier properties (Hu et al., 2016). Additionally, cellulose whiskers have been prepared from dewaxed and alkali-treated rice husk in a multistep environmentally friendly process involving bleaching with hydrogen peroxide/tetra-acetythylenediamine, and further delignification with a mixture of acetic and nitric acids (Rosa et al., 2012). The resulting cellulose has high purity and crystallinity, and can be hydrolyzed with sulfuric acid to produce elongated rod-like whiskers. Also, a combined homogenization-high intensity ultrasonication process has been developed by Dilamian and Noroozi (2019) to produce nanofibers from rice straw with uniform morphological structure, diameters 6–20 nm, and an aspect ratio of ~177. These fibers have good thermal stability, and a number of potential uses.

Nanofibrillated cellulose with long structures 30–200 nm wide and excellent water retention and swelling capacity can be produced by pretreating rice straw by high-density steam flash-explosion followed by successive enzymatic treatments with xylanase, laccase, and cellulase (Yan et al., 2018). Then by grafting hydrophobic groups, a product is generated that can function as high-quality dietary fiber with strong ability to absorb oil and help regulate body weight; it also had other potential health benefits, including adsorption of bile acids, cholesterol, and nitrite ion.

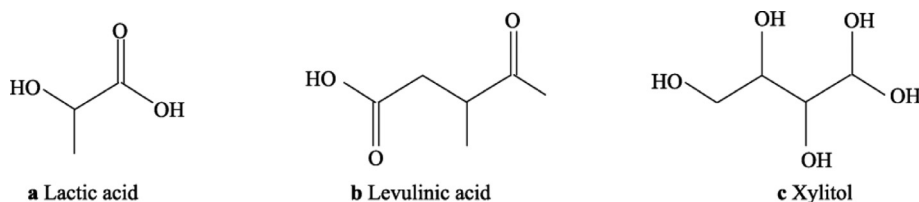


Fig. 5. Chemical structures for (a) lactic acid, (b) levulinic acid, and (c) xylitol.

6.2.3. Textile, paper and cardboard production

Cellulose is the main component of paper and textiles derived from plant fibers, although rice straw and husks are not used extensively in paper production, and the uses of cellulose and cellulose acetate in textiles are well-known and are not considered in this review. However, Jeetah et al. (2015), report that a blend of rice husk, bagasse and waste paper can produce cardboard suitable for packaging as corrugating medium, wrapping, and insulating board, and recently, composites formed from rice straw modified by in situ polymerization of ammonium polyphosphate polyelectrolyte and high-density polyethylene have been described as materials with good flame retarding properties (Jiang et al., 2018).

6.2.4. Other uses of cellulose from rice waste

Cellulose properties can be changed by derivatization with different chemical groups (Heinze et al., 2018). Hydrophobicity is increased by esterification (Lin et al., 2018; Trinh and Mekonnen, 2018), and pH sensitivity is conferred by cationization (Sun et al., 2019). It can be converted to cellophane (McKeen, 2017), which is used in food packaging as a transparent sheet with low permeability to air, oils, bacteria, and water, and cellulose acetate (Biswas et al., 2006), which also has uses as solid plastics, film, and food wrapping products.

6.3. Substrates for enzyme production

Although microbial fermentation is used in the production of ethanol and lactic acid, the same processes can be used for enzyme production. For example, an extracellular laccase has been extracted from the rice blast fungus *Magnaporthe grisea*, and can oxidize a wide range of substrates, although it is strongly inhibited by Cu-chelating agents (Iyer and Chattoo, 2003). White rot fungi of the *Marasmius* sp. produce laccase by solid state fermentation of rice straw and other agricultural wastes (Risdiyanto et al., 2012), and *Aspergillus heteromorphus* can be used to produce enzymes by solid state fermentation of rice straw and husks after alkali treatment and microwave irradiation (Singh et al., 2011); here cellulase and xylanase production preceded that of manganese peroxidase and laccase. Interestingly, Dhillon et al. (2011) found that production of cellulase, β -glucosidase, endoglucanase and xylanase from rice straw supplemented with wheat bran was greater with mixed cultures of *Aspergillus niger* and *Trichoderma reesei* than with either as a monoculture, and thus demonstrated a synergistic microbial effect.

6.4. Production of speciality organic chemicals

6.4.1. Lactic and levulinic acid production

Rice straw and husks represent cheap materials for the preparation of lactic acid (Fig. 5a) for the pharmaceutical, food, and chemical industries by fermenting enzymatically hydrolyzed lignocellulosic material with *Lactobacillus casei* (Qi and Yao, 2007). Addition of non-ionic surfactants and poly(ethylene glycol) increased conversion of cellulose into fermentable sugars, and addition of Tween improved lactic acid production (Yao et al., 2007). Lactic acid can also be produced from rice straw or husks by *Lactobacillus rhamnosus* (Huy and Khue, 2016; Montipó et al., 2016), and by alkaline hydrothermal conditions in presence of NiO nanoplates (Younas et al., 2016). Rice straw can be converted to ethyl lactate with ethanol in the presence of Lewis and Brønsted acids with both acid systems contributing to ethyl lactate production (Younas et al., 2019); the Brønsted acid sites facilitate degradation of holocellulose into monosaccharides, whilst the Lewis acid sites catalyze C—C bond cleavage and rearrangement reactions during isomerization, retro-aldol and finally esterification reactions.

Levulinic acid (Fig. 5b) is produced by acidic depolymerization of rice husks (Bevilaqua et al., 2013); glucose is formed as an intermediate, then dehydrated to 5-hydroxymethylfurfural from which levulinic acid is generated. Also, acid hydrolyzed rice husks are a source of succinic acid by fermentation with *Actinobacillus succinogenes* (Bevilaqua et al., 2015).

6.4.2. Xylitol production

Xylitol (Fig. 5c) is a five carbon sugar alcohol that is widely used in the food and pharmaceutical industries and as a sweetener for diabetics. Although it is currently produced chemically on a large scale by Ni-catalyzed xylose hydrogenation, the process is expensive (Venkateswar Rao et al., 2016). Therefore, microbial production could be a cheaper alternative, and the various processes involved in bioconversion of lignocellulosic biomass to xylitol have been reviewed by de Albuquerque et al. (2014).

Yeasts of the genus *Candida* are good xylitol producers, and involve the enzymes d-xylose reductase which reduces d-xylose in hemicellulose hydrolysates to xylitol, and xylitol dehydrogenase which reoxidizes xylitol to d-xylulose. Production of xylitol from rice

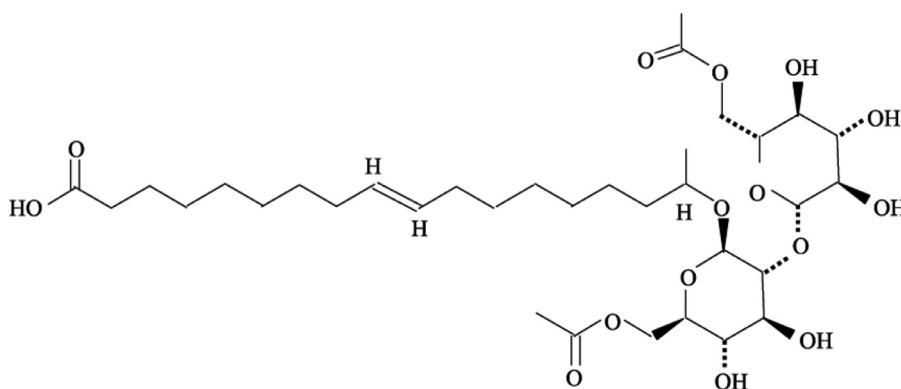


Fig. 6. Representation of a sophorolipid structure.

straw hemicellulose hydrolysate with *C. subtropicalis* immobilized in polyacrylic hydrogel thin films has been described by Liaw et al. (2008), and Swain and Krishnan (2015) have described a sequential fermentation process using *C. tropicalis* for the combined production of ethanol and xylitol from rice straw pretreated with aqueous ammonia to decrease the amount of lignin and improve enzymatic digestibility of rice straw. Xylitol can also be produced from hemicellulosic hydrolysates of rice straw and other agricultural residues by a recombinant *Saccharomyces cerevisiae* strain that expresses cytosolic xylose reductase, along with β -glucosidase, xylosidase, and xylanase enzymes (Guirimand et al., 2016). No addition of commercial enzymes is required, and all of the yeast enzymes contribute to consolidated bioprocessing of the lignocellulosic hydrolysate.

6.4.3. Lignin-derived chemicals

Valuable phenolic compounds can be produced by hydrothermal liquefaction of rice straw, and then separated on a commercial adsorption resin XAD-4 modified by α, α' -dichloro-*p*-xylene (Chen et al., 2015). Recently, Sun et al. (2018) reviewed the functionalization or defunctionalization of lignin-based compounds, and potential applications of such emerging new structures for the synthesis of biobased polymers or pharmacologically active molecules. Furthermore, phenolic acids extracted from rice straw represent a cheap source of antimicrobial compounds, as seen by their strong inhibitory effect on *Staphylococcus aureus* (Cui et al., 2019), which was attributed to peroxides generated from a combination of *p*-coumaric and ferulic acids. A strong inhibitory effect on *Botrytis cinerea* in tomato has also been reported by Hou et al. (2020), who showed that addition of phenolic acids increased phenylalaninammonia lyase and polyphenol oxidase activities, and decreased peroxidase and catalase activities in infected leaves as oxidative stress was reduced.

6.4.4. Production of sophorolipids

Sophorolipids (Fig. 6), are a type of glycolipid with medicinal and cosmetic potential (Morya et al., 2013), that are synthesized by some yeast species, and can function as environmentally friendly alternatives to petrochemical-derived surfactants. As an example, production of sophorolipids in high yield from rice straw holocellulose hydrolysate by fermentation with *Wickerhamiella domercqiae* has been described by Liu et al. (2016).

6.5. Biological control

6.5.1. Algal control using rice straw

Addition of activated rice straw has been reported to produce an appreciable decrease in microalgae in water, and this was interpreted as due to synergistic effects of humic substances and H_2O_2 produced by straw decomposition (Rubeena et al., 2014). In another study, Eladel et al. (2019) showed that water and methanol extracts of rice straw inhibit the cyanobacterium *Anabaena* sp., but stimulate *Chlorella* sp. Thus although rice straw extracts represent cheap and eco-friendly material for control of the growth of *Anabaena* sp., they may not be effective with some other cyanobacteria and microalgae.

6.5.2. Insecticidal properties

Nano and ground sized particles of rice husk have been reported to show insecticidal effects against the greater wax moth, *Galleria mellonella* (Shebl et al., 2020). Nanosize particles were more potent than the ground rice chaff alone, and activity was associated with the high silica content, which resulted in disturbances in the biological patterns of both juvenile and adult stages.

6.6. Production of speciality materials

6.6.1. Bioplastics

A new bioplastic with potential use as shrink films and sheets or for shape memory effects has been produced from rice straw using a Naviglio extractor followed by dissolution in trifluoroacetic acid. Its mechanical properties in the dry state are comparable to those of polystyrene, whilst cast bioplastic in the wet state behaves similarly to plasticized poly(vinyl chloride) (Bilo et al., 2018).

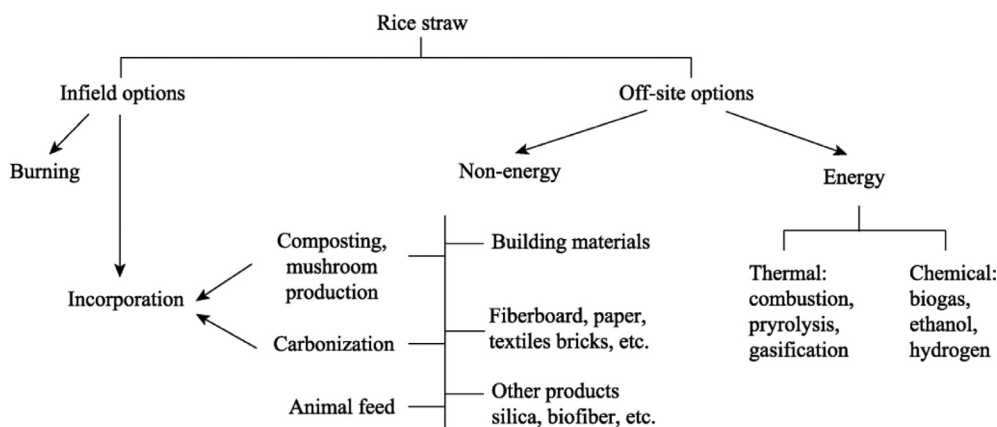


Fig. 7. Summary of main options for use of rice straw.

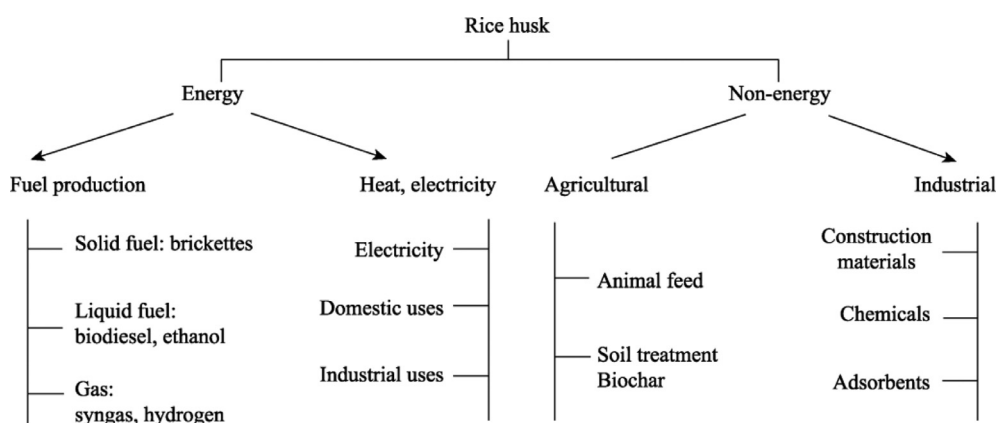


Fig. 8. Summary of main options for use of rice husk.

6.6.2. Silicon carbide

Rice husk can be converted into silicon carbide by pyrolysis or in a plasma reactor. The latter has the advantage of continuous production, and generates high quality silicon carbide suitable for use in semiconductors (Nayak et al., 2005). Pretreatments that have been used successfully to improve silicon carbide quality include: (1) acid leaching to decrease the impurities in the silicon carbide; (2) enzymatic treatments to remove excess carbon to obtain the optimum silicon to carbon ratio for the reaction; and (3) addition of a catalyst, such as FeSO_4 , Fe and Ni oxides or nitrates, CoCl_2 , and sodium silicate.

6.6.3. Precursor for biological implants

The β -wollastonite produced from a mixture of rice straw or husk ash and limestone has a porous structure with significant Ca, P and Si content (Ismail et al., 2016; Shamsudin et al., 2016). These aid the formation of amorphous calcium phosphate and calcium deficient hydroxyapatite on its surface with bioactivity properties that make it suitable for use as dental and other implants.

6.6.4. Rice straw based solar steam generation device

A robust still for solar steam generation has been described by Fang et al. (2019). This consisted of a composite of carbonized upper leaves of rice straw and bacterial cellulose, which functions as a sunlight absorber, whilst the lower culms function as water pumps. This rice straw-derived solar still has potential for sustainable clean water production, and can be used with any water-bearing media.

6.6.5. Electronics products

Activated carbon from rice husk can be used as an active material in an electric double layer capacitor using a three-dimensional (3D) porous current collector (Kuratani et al., 2011).

7. Safety issues for handling rice husk

Finally, I wish to recommend the exercise of caution when working with rice husk residues, which invariably contain fine dust particles that are formed during processing. These can irritate the upper respiratory tract, and result in allergic reactions, rhinitis,

asthma, bronchitis, chronic obstructive pulmonary disease, and extrinsic allergic alveolitis, so breathing filters should be used when handling such materials. Furthermore, the particles in rice husk dust are easily ignited. They can smolder on hot surfaces (El-Sayed and Khass, 2013), and have the ability to form explosive concentrations in air (Korotkova et al., 2016). Therefore, standard precautions for handling combustible dusts should be used with rice husks.

8. Conclusions and outlook

Rice straw and husks have traditionally been regarded as essentially waste materials of little value. However, increasingly strict regulations governing their disposal have led to scientific efforts to identify potential uses for these materials, and various contributions to agricultural activities, energy generation, environmental pollution control, and construction materials have been identified and developed, and some of the main processes for utilization of rice straw and husks are summarized in Figs. 7 and 8. However, these lignocellulosic materials have other potential uses, and as the science and technology are developed, it is expected that many more uses will be identified in the future as societies increase their emphasis on sustainability. It is also anticipated that many uses will be in relatively small scale operations, especially if countries adopt a policy of rural development as a mechanism to decrease the rate of urbanization, and utilization of the science may be determined by non-scientific factors, the principal of which concerns the economics of the various types of process. However, ultimately final decisions on particular uses may be political through either the use of taxation or legislation to promote one type of activity over another, and it is expected that certain traditional activities, such as the burning of straw will be progressively phased out as a result of legislation that makes alternative uses more attractive.

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