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Review

Potential of rice straw for bio-refining: An overview

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HIGHLIGHTS

- Availability and cultivation practices of paddy rice.
- Overview on the production of value added products from rice straw.
- Recent developments in rice straw based biorefinery.

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ABSTRACT

The biorefinery approach for the production of fuels and chemicals is gaining more and more attraction in recent years. The major advantages of biorefineries are the generation of multiple products with complete utilization of biomass with zero waste generation. Moreover the process will be economically viable when it targets low volume high value products in addition to high volume low value products like bioethanol. The present review discuss about the potential of rice straw based biorefinery. Since rice is a major staple food for many Asian countries, the utilization of the rice straw residue for fuel and chemicals would be very economical. The review focuses the availability and the potential of this residue for the production of fuel and other high value chemicals.

Contents

1. Introduction

Rice is one of the most important agricultural crops in Asia. In terms of production rice is the third most important grain crop in the world behind wheat and corn (Binod et al., 2010). Rice straw is an important residue which is generated in large amount in Asia. Every kilogram of grain harvesting is accompanied by the production of rice straw to a tune of 1.0–1.5 kg (Maiorella, 1985). Major proportion of the rice straw is burnt in the field itself. Burning of rice straw in the open fields leads to air pollution and also release

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particulate matter into the atmosphere. In India 23% of rice straw residue produced is surplus and the green house gas emissions through open field burning constitute 0.05% (Gadde et al., 2009). There are two major types of residues from rice cultivation- rice straw and rice husk. Straw represents the residue left out after grain harvesting and it includes stem, leaves and spikelets. Rice straw has been traditionally used as animal feed and as well as feed stock for paper industry and organic fertilizer. Straw can be ploughed into the soil or burnt in the field.

Bio-refinery involves the continuous processing of biomass into a range of products and energy without any wastage of biomass feed stock. This will lower the environmental impact and improve the overall economics (El Mekawy et al., 2013). Crop based bio-refineries are gaining potential importance in recent years and several pilot scale plants were available and several research and developmental activities were going on for the development of fully fledged systems. Most of the existing cereal based bio-refinery use dry cereals as raw materials. These were used for first generation biofuels. Second generation biofuels are produced from lignocellulosic biomass like straw residues.

This review discusses potential of rice straw as well as possibilities and challenges associated with rice straw based biorefinery and its commercialization aspects.

2. Potential of rice straw

Rice straw generated after grain harvesting is currently used or disposed by ploughing into fields, compost, animal feed, cattle house flooring, straw handicrafts, covering material for fields as well as for combustion (Matsumura et al., 2005). Pyrolysis of rice straw produces liquid (bio-oil), solid (bio-char) and mixture of light gases (syngas). Compounds of bio-oil from rice straw contain furans, phenols, aromatics, alcohols, ketones, acids and pyranoglucose. Pyrolysis temperature has a profound effect on product yield. Alcohol and pyranoglucose were the products of cellulose pyrolysis while ketones were derived from hemicelluloses pyrolysis.

Rice straw can also be used for the production of second generation biofuels. Several reports were there on utilization of rice straw for the production of second generation biofuels (Yoswathana et al., 2010; Wi et al., 2013; Belal, 2013; Abo-State et al., 2014). Since cellulose is embedded in the lignin matrix, some pretreatment to be carried out to make cellulose accessible for enzymatic saccharification (Wi et al., 2013). Several pretreatments are currently available which includes physical, chemical, biological and hybrid processes for effective hemicelluloses and lignin removal.

Biogas can be produced from rice straw by anaerobic digestion (Song et al., 2012). Anaerobic digestion of rice straw is a green technology since it produces better option for waste utilization as well as reducing green house gas emissions by being a substitution for fossil fuels (Murphy and Power, 2009). Anaerobic digestion involves four major steps – hydrolysis, acidogenesis, acetogenesis and methanogenesis.

Several reports were available for the effective utilization of rice straw for the preparation of composite (Buzarovska et al., 2008; Wu et al., 2009; Basta et al., 2011; Kalagar et al., 2011).

Rice straw-cement bricks find suitable applications as load-bearing walls (Basta et al., 2011). Pretreatment of rice straw with alkali results in an increase in interfacial adhesion between rice straw flour and polypropylene thereby improving the mechanical properties (Kalagar et al., 2011). Rice straw reinforced polypropylene composites showed improved properties in presence of 5% rice straw micro fibril (Wu et al., 2009).

Pretreated rice straw serves as an excellent source for the production of different industrially important enzymes (Rahnama et al., 2013; Zahari et al., 2016). Alkali pretreated rice straw was used for the production of cellulases and xylanases by *Trichoderma harzianum* SNRS3 (Rahnama et al., 2013). They utilized alkali pretreated rice straw for the production of cellulases and xylanases by *T. harzianum* SNRS3 under solid state fermentation. The study revealed that rice straw serves as a better inducer for the production of cellulases and xylanases without addition of any chemicals.

Rice straw is used as a source of energy in various parts of the world. It is used as fuels for cooking food and warming room by direct burning (Liu et al., 2011). Garba and Zangrina (2015) explored the potential of rice straw and husk as potential sources for mini-grid rural electricity in Nigeria. The study revealed that 1.3 million MW h y^{-1} of electricity can be accessed from rice straw. Access to grid electricity is unavailable in many Nigerian villages. This study seems promising for exploitation of rice straw for electricity generation. Lactic acid serves as building blocks and finds wide applications in food, biopolymer (polylactic acid – PLA) and pharmaceuticals. Yao et al. (2007) reported lactic acid production from rice straw by simultaneous saccharification and fermentation of pretreated rice straw. Addition of surfactant improved the lactic acid production.

2.1. Composition

Chemical composition of biomass is important and it varies with seasons as well as with variety. Variation is considered as a disadvantage since it affects the consistency and yield of end products. Compositional analyses as well as structural characterization are the key factors that affect efficiency of its utilization. Hence structural characterization of the components of rice straw is essential (She et al., 2012).

Lignin is a major cell wall component and is an amorphous polymer composed of three aromatic alcohols – *p*-coumaryl, coniferyl and sinapyl alcohols (Lewis and Yamamoto, 1990). Lignin does not exist in plant tissue as an independent polymer and it is always seen associated with other plant polymers like cellulose and hemicelluloses through covalent bonds. Lignin/phenolics–car bohydrate complexes of herbaceous plants contain different amounts of lignin and carbohydrates. Carbohydrate–lignin complexes of rice straw contains 63.9% of carbohydrates, 2.8% uronic acid, 27.7% Klason lignin, 4.2% acetyl content, 4% trans-*p*-coumaric acid and 0.8% trans-ferulic acid (Azuma and Koshimjima, 1988).

Rice straw contains *p*-coumaric acid and ferulic acids in their esterified and etherified form and the content of ester linked *p*-coumaric acid is lower and ether linked *p*-coumaric acid is higher in rice straw when compared to corn and wheat (Sun and Tomkinson, 2002). The content of ferulic acid is also higher in rice straw. Rice straw is poor in nitrogen but rich in inorganic compounds. Rice straw contains high ash content (10–17%) (Zevenhoven, 2000) and also high silica content in ash (SiO_2 is 75%) and low alkali content in ash (less than 15%) (Baxter et al., 1996).

2.1.1. Rice straw availability

Rice has been cultivated in Asia since 6500 BC. Rice is now naturalized in most tropical, subtropical and Mediterranean regions. Rice straw is the vegetative part of the rice plant cut at grain harvest and is the major forage in rice-producing areas. Rice straw yield can be estimated based on the grain production by applying a straw: grain ratio. About 1.0–1.5 kg of straw is produced per kg of grain harvested (Maiorella, 1985).

The yield of rice varies widely among countries due to varieties used for cultivation, climatic conditions and cultivation practices. Asia is contributing 91% of world rice production and remaining 5% from the Americas, 3% from Africa and 1% from Europe and

Table 1
Cultivated agricultural area and rice production in different regions of the world, and estimate of rice straw production. (Data based on FAO grain production data of 2014. Data are ranked by rice production.)

Country	Paddy rice cultivation area (million hectares)	Paddy rice production (million metric tonnes)	Paddy straw production (million metric tonnes)
China	30.60	208.23	208.23–312.34
India	43.40	157.20	157.20–235.8
Indonesia	13.79	70.84	70.84–106.26
Bangladesh	11.82	52.23	52.23–78.34
Vietnam	7.81	44.97	44.97–67.45
Thailand	10.83	32.62	32.62–48.93
Myanmar	6.79	26.42	26.42–39.63
Philippines	4.73	18.96	18.96–28.44
Brazil	2.34	12.17	12.17–18.25
Japan	1.57	10.54	10.54–15.81

Oceania (Binod et al., 2010). The major rice cultivating countries from Asia are china, India, Indonesia, Bangladesh, Myanmar, Thailand, Vietnam, the Philippines, Japan, Pakistan, Cambodia, the Republic of Korea, Nepal and Sri Lanka (Muthayya et al., 2012). Other major non-Asian rice producing countries include the United States, Brazil, Egypt, Madagascar and Nigeria, which together account for 8% of the rice produced globally. Rice is currently grown in different countries and the world dedicated 163.24 million hectares for rice (FAO, 2014). The top ten paddy rice producing countries in the world are China, India, Indonesia, Bangladesh, Vietnam, Thailand, Myanmar, Philippines, Brazil and Japan (FAO, 2014). Worldwide production of paddy rice has risen steadily from about 200 million tonnes in 1960 to over 740.95 million tonnes in 2014 (FAO, 2014). The average world farm yield for rice was 4.53 tonnes per hectare (FAO, 2014). The estimated rice straw production amounts to approximately 740.95–1111.42 million tons per year globally (Table 1).

China and India alone contributes nearly half of the world output (FAO, 2014). China is the world's largest rice producer (208.23 million metric tons), which accounts for as much as 28% of total world rice production. Rice production in China is an important part of the national economy. More than 90% of the rice area in China is irrigated and few areas being cultivated under rain fed conditions. China is the world leader in hybrid rice production. In the late 1970s, China was the first country to effectively produce hybrid rice for agriculture in temperate climatic conditions. Yield of hybrid rice is 15–20 percent more than conventional rice. India is considered to be one of the original centres of rice cultivation. Rice is grown widely across the nation in an area of over 44 million hectares. This rice harvesting area is the largest in the world and covers more than 20 states in India. Out of these states, top 10 rice producing states account for around 80% of total rice production in India. West Bengal is the highest rice producing state in India with more than 13% contribution in rice production. The Indian state showing highest yield in rice production is Tamil Nadu with yields of more than 3900 kg per hectare. In India rice-based production systems provide the major source of revenue and employment for more than 50 million households. In tropical climates having sufficient water availability can grow more than one crop of rice per year so straw is generated more than once a year.

2.1.2. Rice varieties

The word "rice" generally indicates a plant of the species *Oryza sativa* L. The genus *Oryza* L. in the grass family Poaceae (Gramineae) is classified under the tribe Oryzeae, subfamily Oryzoideae (Lu, 1999). The *Oryza* genus is thought to have originated about 14 million years ago in South East Asia. It has then evolved, diversified and spread into wild *Oryza* species and distributed throughout the tropics (Huang et al., 2012). Rice has approximately 22 species of the genus *Oryza*, of which 20 are wild species and distributed throughout the tropics and subtropics (Vaughan, 1994).

The two important species of rice for human consumption are *O. sativa* L. and *Oryza glaberrima* Steud. Both are developed as a result of growing them over many centuries and by selecting the important traits (Molina et al., 2011). The Asian cultivated rice (*O. sativa*) is actually cultivated worldwide, while *O. glaberrima* is only cultivated in a few countries in Africa. About 3000 years ago, people lives in the floodplains of the Niger River in Africa domesticated *O. glaberrima* from its wild ancestor *Oryza barthii* (Linares, 2002), several characteristics such as brittle grains and poor milling quality of *O. glaberrima* shows that it is less suitable for cultivation compared to *O. sativa*. *O. glaberrima* also has lower yields than *O. sativa*, but it shows high tolerance to fluctuations in water availability, metal toxicity, soil infertility and extreme climatic conditions. It also shows better tolerance to various pests and diseases.

In China, between 8200 and 13,500 years ago, *O. sativa* (Asian rice) was first domesticated from the wild rice *Oryza rufipogon* and then spread to South and Southeast Asia (Normile, 1997). Now, *O. sativa* rice is widely cultivated on every continent except Antarctica. There are above 40,000 varieties of cultivated rice (*O. sativa*) said to exist but the exact figure is uncertain. More than 90,000 samples of cultivated rice varieties and wild species are stored at the International Rice Gene bank and these are used by researchers from the world.

O. sativa, can be categorised into four main groups: *indica, japonica, aromatic* and *glutinous*.

2.1.2.1. Japonica rice. Japonica is a collection of rice varieties from northern and eastern China and extensively growing in some areas of the world. It is found in the cooler areas of the subtropics and in the temperate zones. It accounts for more than 10% of global rice trade. It is a short plant with narrow, dark green leaves and medium-height tillers. The grains are round and do not easily break. The low amylose content, making them moist and sticky when cooked. Japonica varieties are usually grown in dry fields, in temperate East Asia, high elevations in South Asia and upland areas of Southeast Asia.

2.1.2.2. Indica rice. Indica rice is usually grown in hot climates of tropics and subtropics. It accounts for more than 75% of global trade. Indica plants are tall with broad to narrow, light green leaves. The grains are long to short, slender, somewhat flat, and tend to break easily. When cooked, due to high amylose content the rice is fluffy and not showing any sticky nature. Most of the rice produced in Southern Asia, Thailand, Vietnam, including Sri Lanka, India and Southern China is Indica rice.

2.1.2.3. Aromatic rice. It is a medium to long-grained rice. It is known for its nut-like aroma and taste which is caused by a chemical compound 2-acetyl-1-pyrroline. Varieties of aromatic rice include: jasmine, basmati, texmati and wehani. When cooked, the grains have a light and fluffy texture.

2.1.2.4. Glutinous rice. It is also called as sweet rice, sticky rice and waxy rice. It is a type of short-grained Asian rice that is sticky in nature when cooked. Glutinous rice is distinguished from other types of rice by having lesser amounts of amylose and high amounts of amylopectin. Amylopectin is the basis of sticky quality of glutinous rice. Glutinous rice is grown in Laos, India, China, Japan, Korea, Indonesia, Myanmar, Vietnam, Malaysia, Taiwan Thailand, Bangladesh, Cambodia and the Philippines.

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2.1.3. Rice cultivation practices

Rice grows in a wide range of environmental conditions and is productive in many situations. Different classifications of rice environments are mainly based on altitude (upland vs. lowland) and water source (irrigated or rain fed) (IRRI, 1970).

Worldwide, 75% of the rice production comes from 80 million hectares of irrigated lowland (Maclean et al., 2002). Irrigated rice is growing in bunded fields or paddies, which are surrounded by a small edge that keeps 5–10 cm of water on the field. In irrigated lowland system, rice is grown continuously with two or even three crops a year. So this system remains the most important rice production systems for food security in tropical and subtropical areas, particularly in Asian countries. Rain fed lowland rice is grown in river deltas and coastal areas. Rain fed lowland system using bunded fields that is flooded with rainwater for at least part of the cropping season. About 20% of the world's rice production is contributed by 60 million hectares of rain fed lowlands. Rain fed rice is usually cultivated under many abiotic stresses (such as salinity, intensity of rainfall etc.) so yields is unreliable. Rain fed lowland areas show typically very low productivity, with yields of 1–2.5 t/ha. Rainfed lowland rice predominates in areas of South Asia, parts of Southeast Asia, and essentially all of Africa. Upland rice contributes only about 4% of the world's total rice production (Gupta and Toole, 1986). Upland environments are highly heterogeneous at altitudes up to 2000 m, with climates ranging from humid to sub-humid, soils from relatively fertile to highly infertile and landscape from flat to steeply sloping. Rainfed upland rice covers large areas but, because of many constraints, these areas show typically low productivity with yields of about 1 t/ha. Almost two-thirds of the world's total upland rice area is located in Asia. China, India, Bangladesh, Cambodia, Indonesia, Myanmar, Thailand and Vietnam are major upland rice producers (Tuong et al., 2005). Cultivation practice of Indica rice varieties in major rice producing countries (Asian countries) can be classified in to three stages; pre-planting, growth and harvest.

2.1.3.1. Pre-planting. The major pre-planting activities are preparation of crop calendar, land preparation and seed selection. A crop calendar for rice cultivation allows better planning of all farm activities. Cropping calendar is a schedule of the rice growing season from the land preparation, to crop establishment and maintenance (weeding, fertilizing) to harvest. The period of time from establishment to harvest is varying among different varieties. So the crop calendar allows a farmer to decide the best time the variety takes from planting to harvest. It may vary little depending on the growing conditions particularly water availability and solar radiation. Normally short duration varieties take a period of 100–120 days, medium duration 120–140 days and long duration 160 days plus. Before rice can be planted, the soil should be in the best physical condition for crop growth. Land preparation involves ploughing and harrowing to mix and level the soil. Farmers can till the land by animals or tractors and other machinery. Next, the land is levelled to reduce the amount of water wasted by uneven areas of too-deep water or exposed soil. Effective land levelling allows the seedlings to become established more easily and increases both grain quality and yields (IRR1, 2013).

Seed must be grown, harvested and processed correctly for best yield and quality products. Quality seed can improve yields by 5–20%. Using good seed leads to lower seeding rates, higher crop emergence, more uniform plant stands and more vigorous early crop growth. Good seed is pure of chosen variety, uniform in size and viable for more than 80% germination with good seedling vigour. Seed vigour refers to the seed's level of activity and performance during germination and seedling emergence. Seeds showing low vigour are generally produce weak seedlings that are susceptible to environmental stresses. On the other hand, seeds that are high in vigour produce healthy and uniform seedlings, which give them a competitive advantage against environmental stresses. Vigorous growth in early stages reduces weed problems and increases crop resistance to insect pests and diseases. High quality seeds are free from factors that reduce germination and seedling vigour like weed seeds, seed-borne diseases, insects, pathogens, various types of mechanical injury and other external matter (IRR1, 2013).

2.1.3.2. Growth. Various activities during growth are crop establishment, water management, nutrient management and crop health. Rice crops can either be direct seeded or transplanted. In direct seeding, seeds are sown directly in the field. Direct seeding involves broadcasting dry seed or pre-germinated seeds and seedlings by hand or planting them by machine. In rain fed ecosystems, dry seed is manually transmit onto the soil surface and then incorporated by ploughing. While in transplanting, seedlings are first raised in seedbeds before they are planted in the field. In irrigated areas, seed is normally pre- germinated prior to transferring. Pregerminated seedlings from seedbed are transferred to the wet field. Transplanting is the most popular plant establishment technique across Asia. It requires less seed and is an effective method to control weeds, but requires more labour. The best time to plant depends on variety, region, climate, water availability and the best harvest time. Rice is extremely sensitive to water shortages and good management practices are critical to maximize water efficiency and yield. Continuous flooding of water generally supplies the best growth environment for rice. After transplanting, initial water levels should be around 3 cm, and with increasing plant height water level should gradually increase to 5–10 cm and remain there till the field is drained 7–10 days before harvest. Continuous flooding helps ensure sufficient water and control weeds. In an irrigated lowland production system rice plant takes 1432 L of water to produce 1 kg of rice. Optimal amount of water needed for irrigated rice in Asia is around 1300–1500 mm. Worldwide, water for agriculture is becoming increasingly insufficient. Rice is extremely sensitive to water shortages due to its semi-aquatic ancestry (IRR1, 2013).

Rice plant has specific nutrient needs in each growth stage and this makes nutrient management a critical aspect of rice farming. Because of prolonged flooding in rice fields, farmers are able to preserve soil organic matter and also receive nitrogen freely from biological sources, which means they need little nitrogen fertilizer to retain yields. However, farmers can tailor nutrient management to the specific environment of their field to increase yields (Dobermann and Fairhurst, 2000). The rice plant has a wide array of predators and pathogens in the field. These include harmful insects, rodents, viruses, diseases and weeds. Every year farmers lose a percentage of their rice crop due to pests and diseases and is managed through the application of pesticides. Weed control is important to prevent losses in yield and to obtain good grain quality. Specifically, weeds reduce yields by direct competition for nutrients, sunlight and water. Farmers manage weeds through water management and land preparation, by manual weeding and by herbicide application. Along with good crop management, timely and precise diagnosis can significantly reduce losses.

2.1.3.3. Harvesting. Harvesting is the process of collecting the mature rice crop from the field. Paddy harvesting process includes reaping, stacking, handling, threshing (separating the paddy grain from the rest of cut crop), cleaning and hauling. Good harvesting methods are essential to maximizing grain yield and minimizing quality deterioration. Harvesting systems vary from region to region. A wide variety of traditional tools or combine harvesters may be used for harvesting. Manual harvesting with simple hand tools like sickles and knives is common across Asia. Manual harvesting is labour intensive but very effective when a crop has lodged or fallen over. Manual harvesting requires 40–80 h per hectare and it takes extra labour to manually collect the harvested crop. Mechanical harvesting using harvester is the other option, but not so common in developing countries due to the availability and cost of machinery (IRR1, 2013).

3. Biorefinery concept

Biorefineries are the future of biomass processing as they can generate multiple products from biomass. It is associated with upstream, mid-stream and downstream processing of biomass into variety of products. Thus biorefineries will act as analogues to petroleum refineries where a range of chemicals or products are made from the biomass using different process configurations. In general, biorefinery approach is expected to improve the economics of the overall biomass conversion process as it generates multiple products from the biomass rather than single product which is bioethanol. Biorefinery approaches of lignocellulosic biomass have been studied by Kadam et al. (2008) where the corn stover was converted into ethanol and the dissolving pulp and lignin were used in resin production. A biorefinery process based on bioethanol, biogas and biohydrogen from wheat straw was assessed by Kaparaju et al. (2009). Luo et al. (2010) investigated the biorefinery concept of lignocellulosic materials where ethanol is considered as the bulk fuel, succinic acid as the major chemical, acetic acid production from mixed acid fermentation as by-product. Process wastes were used for steam and electricity generation. System analysis study of this proposed biorefinery was much better than ethanol plant in terms of profit as well as eco efficiency.

Biorefinery is not a new concept as traditional biomass processing can be partially considered as biorefinery. However, the economical drivers such as global warming, insecurities in energy supply and agricultural policies are further expected to improve their operations in a sustainable biorefinery manner. Biorefinery must be able to use wide range feed stocks including forestry, agriculture, aquaculture and residues from industry and households. Based on the products generated from biorefinery it can be classified into energy driven biorefinery (biofuels, power or heat) and product driven biorefinery (biomaterials, lubricants, chemicals, food and feed). The energy driven biorefinery is currently being demonstrated in pilot scale where carbohydrate portion of the biomass is fermented into biofuels and the left over residue which is rich in lignin is used for heat and power generation. The heat and power generation from biomass can be implemented on small to medium scale and can be used as a decentralised system for bioenergy production.

The choice of biorefinery products should be made based on the economics and sustainability of biomass logistics. Biorefinery can mainly be classified into two based on the mode of operation: the thermochemical and biochemical based biorefinery (Fig. 1). Biorefineries based on thermochemical platform include pyrolysis, gasification and liquefaction. Biorefineries based on biochemical platform include pretreatment, hydrolysis and fermentation into ethanol or other values added products. The economic production of liquid biofuels from biomass is a challenge and thus generation of high value compounds can overcome the financial draws associated with liquid biofuel production. Though this approach seems to be promising, careful evaluation of product selection, feed stock availability, location and size of the plant etc. are the factor which determines the economics of the biorefinery.

3.1. Biorefining of rice straw for value added products

The lignocellulosic biomass is recalcitrant in nature. Thus pretreatment is necessary to disrupt the cellulose–hemicellulose–lignin network which can increase the accessibility for subsequent hydrolysis. The solid part left over after pretreatment is rich in cellulose content and is further processed for hydrolysis using enzymes for glucose production and is subsequently fermented to ethanol. The liquor obtained after acid pretreatment/alkali treatment can further be processed into low volume high value products. Utilization of rice straw hydrolysate was assessed for poly-(ϒ-)glutamic (PGA) production using *Bacillus subtilis* NX-2 by Tang et al. (2015). The rice straw hydrolysate rich in xylose (from stage 1) was for cell growth and stage 2 hydrolysate was used for the synthesis of PGA. Batch fermentation of glucose (60 g L^{-1}) or xylose (60 g L^{-1}) as a carbon source resulted in a highest PGA production of 35 g L^{-1} or 26 g L^{-1} after 72 h and 80 h respectively. The study further evaluated the continuous fermentation of PGA production and a maximum PGA production of 73 g L^{-1} was achieved at a productivity of 0.81 g L^{-1} h^{-1} when a total sugar concentration

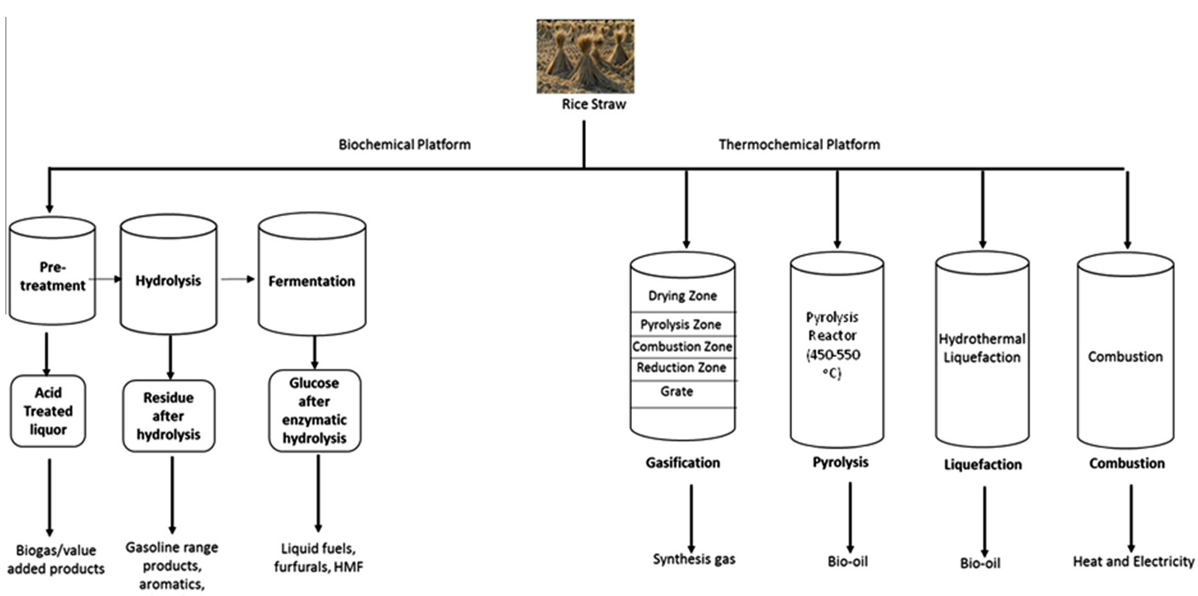

Fig. 1. Classification of biorefinery based on mode of operation.

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of 50 g L^{-1} was added by continuous feeding. A preliminary economic analysis showed approximately 84% or 42% reduction in carbon cost may be achieved if rice straw hydrolysate was used instead of glucose and cane molasses, respectively. Huang et al. (2013) evaluated the 2,3-butanediol production using three different strains (two *Klebsiella* sp. and one *Serratia* sp.) from glycerol and acid pretreated hydrolysate using an integrated biorefinery approach. The enzymatic hydrolysate was successfully fermented into 2,3-butanediol using these three strains. However, when the pretreated hydrolysate was used as a medium for fermentation, the *Serratia* sp. could not ferment as it was unable to convert xylose to 2,3 butanediol. The pretreated hydrolysate was detoxified using $Ca(OH)_2$ over liming or other one was conditioned using NaOH. A maximum Diol yield of 0.39 was obtained when NaOH was used for conditioning the pretreated hydrolysate and was approximately 15% higher compared to $Ca(OH)_2$. Though it is a promising, an industrial scale production of 2, 3 butanediol from pretreated hydrolysate is still in early stage. Further research into scale up, product recovery and downstream processing is essential.

Coproduction of ethanol and xylitol from rice straw pretreated hydrolysate in membrane bioreactor was investigated by Zahed et al. (2015) using the strains of *Saccharomyces cerevisiae* NCIM 3090 with 66.4 g L^{-1} ethanol production and *Candida tropicalis* NCIM 3119 with 9.9 g L^{-1} xylitol production were selected. Xylitol is approximately 4 times valuable than ethanol in the market. When single cultures were used, the concentrations of ethanol and xylitol were 31.5 g L^{-1} and 26.5 g L^{-1} respectively. When used in batch co-culture system, the ethanol and xylitol concentrations were 33.4 g L^{-1} and 25.1 g L^{-1} respectively. The maximum of 55 g L^{-1} ethanol and 31 g L^{-1} xylitol concentration was obtained under continuous co-culture mode at the dilution rate of 0.03 L h^{-1} respectively. Hence, the continuous co-production strategy might be recommended for producing value-added products from rice straw hydrolysate. Hickert et al. (2013) investigated the simultaneous saccharification and co-fermentation of non-detoxified rice hull hydrolysate (RHH) into ethanol and xylitol by *S. cerevisiae* and *Spathaspora arborariae* and using a combination of both. A maximum ethanol yield of 0.45 (g g^{-1}) was achieved and was associated with an ethanol concentration of 10.5 g L^{-1} when RHH based glucose contained acetic acid, furfural and hydroxymethylfurfural. During the co-fermentation of hexose and pentose by *S. cerevisiae* and *S. arborariae* into ethanol and xylitol resulted in the yield of 0.48 and 0.39 (g g^{-1}), corresponding to the concentration of 11 g L^{-1} and 3 g L^{-1}. During simultaneous saccharification and fermentation, the ethanol and xylitol concentrations were reached to a maximum of 14.5 g L^{-1} and 3 g L^{-1}. The study concluded that RHH hydrolysate with both hexose and pentose could be used for ethanol and xylitol production without any detoxification methods.

The separation and concentration of hydroxycinnamic (ferulic and *p*-coumaric acid) acid from rice straw alkaline pretreated hydrolysate was studied by Li et al. (2015) by employing nanofiltration. The study was focused on the effect of operating conditions such as NaCl concentration, pH and permeate flux. A maximum mass percentage of approximately 90% was obtained when rice straw alkaline hydrolysate was treated under concentration–diafil tration mode. Furfural, a value added product from the liquor generated during the steam explosion of rice straw by solid acid catalyst (HZSM-5) was investigated by Chen et al. (2015). A maximum furfural yield of 310 g kg^{-1} was obtained when HZSM was added at 60 g kg^{-1} sugar at a reaction temperature of 160 °C, steam flow rate of 2.5 cm^3 min^{-1} at a total sugar concentration 61.4 kg m^{-3}. This production efficiency was further improved by 21% with the addition of 4-methoxyphenol, a polymerization inhibitor added to the reaction system.

3.1.1. Possibilities and challenges

Recent estimates of biofuel production costs show that second generation biofuels are two to three times more expensive than petroleum fuels on an energy equivalent basis (Carriquiry et al., 2011). To bring down the production cost using biochemical platforms, several challenges need to be addressed to make the biorefinery economically and environmentally competitive. These challenges are in the areas of (i) feedstock production, (ii) feedstock logistics, (iii) development of energy efficient technologies (pretreatment, enzymatic hydrolysis, and microbial fermentation), (iv) co-products development, (v) establishment of biofuel and biochemical standards, (vi) biofuel distribution, (vii) societal acceptance, and (viii) environmental impact minimization. All of these challenging areas require expertise in various sectors like agronomy, biomass logistics, biomass conversion, process engineering, chemistry, conversion technology, genetic engineering, microbial fermentation, economics, and environmental science.

The commercialization and economic viability of a rice straw-based (or any other biomass based) biorefinery is largely dependent on the exploitation of full utilization of biomass components. Biorefinery can take advantage of the multiple components present in the biomass like cellulose, hemicelluloses, lignin and other extractives. The biomass processing intermediates and by products such as furfural, hydroxymethyl furfural and various acids generates during the pretreatment process, can be utilized and hence can maximize the value derived from the feedstock while minimizing the waste. Various types of biorefineries, including whole crop, lignocellulosic and green biorefineries have been proposed or are being developed (Kamm and Kamm, 2004).

There is a vast interest in bio-based processes and products in recent years and these have been placed high on the strategic agenda by many of the industries. This will reflect all industrial sectors. For example, in agricultural sector this will make a rising demand for biomass and it promote agriculture and provide more revenue to the farmers. Similarly, in chemical industry, bio-based innovative products outside the conventional petroleum-based product family trees will confer an advantage to players who manage to find the right molecules and insert them into existing or new value chains. In automobile and aviation industries, biofuels will be an important means to reduce the GHG emission of their fleets to comply with the environmental regulations. In spite of this great relevance in various sectors, there are still numerous technical, strategic and commercial challenges that need to be overcome before any large-scale commercialization of the industry can succeed.

The most important challenge is the technology. Biorefineries have to employ best technologies in each unit operations like pretreatment, hydrolysis, fermentation and even storage of biomass and end products. This requires lots of inputs and expertise from various sections starting from the farmers to engineers and scientists. The success of a biorefinery will be evaluated by the net energy that is produced using the different processing steps (von Blottnitz and Curran, 2007). It is widely reported in several techno-economic evaluations of second generation biorefineries that lignin will be a good energy source for different processing steps. Establishing biorefineries near thermal plants (coal or nuclear plant) or using energy from renewable resources (wind, solar, geothermal, etc.) is another option to get heat and power. Adding an anaerobic digestion facility adjacent to a biorefinery will be beneficial that could clean waste water and at the same time the biogas generated could be used for different biorefinery operations (Balan, 2014).

Another significant challenge is to establish the necessary infrastructure. Proper supply chain and distribution infrastructure should be planned well. High capital cost is required for the machinery and

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its installation. So the involvement of government and public funds may be required to meet the high capital cost of a biorefinery, if the private company is beyond the financial reach.

Government policies need to be directed to promote the biofuels and green technologies in order to overcome these challenges effectively. Environmental protection and energy security should be the topmost priority and government also need to ensure the food security and avoid land-use change due to the promotion of biomass based biorefineries. Petroleum companies also need to promote petroleum-replacement by biofuels and take risk and explore the new business opportunities. Consumers also need to be educated about the benefit of bio-based products. The environmental sustainability and business opportunities of bio-based processes and products need to be well spread among the business consumers and common man. NGOs and public authorities must be involved from an early stage to ensure development of the industry in a manner compatible with the highest environmental and social standards. Without these, broad public acceptance and the adoption of bio-based products will be hard to accomplish.

3.1.2. Commercialization

The biorefinery industry is gaining a positive pace during the last five years and most of the second generation plants are expected to be ready for large scale commercial production in a few years. Many of the plants are already commercialized the bioethanol production and most them are diversifying the products in a biorefinery concept. Today's biorefinery technologies are based on the utilization of whole plant and on the integration of traditional and modern processes for utilization of biological raw material.

In Asian countries where rice is a staple food, rice straw is a promising biomass for the production of fuels and chemicals. Several studies on techno-economic evaluation of small-scale ethanol production units from rice straw show the technical and economical viability (Tewfik et al., 2010; Diep et al., 2012). The techno-economic analysis of a straw-based biorefinery for power, heat, pellet and bioethanol located in Sweden shows a feasible economic configuration, having an over 30% production cost reduction compared with the conventional cogeneration plants of bioethanol and solid fuel.

Based on pilot scale studies it was proved that biorefining can be successfully used for the production of commercial products. Without competing with food production, wheat straw and rice straw can be converted into plastics, adhesives or resins (BIOCORE, 2014). In near future, several industries would be investing in the setting up of a biorefinery based on rice straw and it would be commercial reality. The study shows that straw must be properly pre-treated in order to guarantee the quality of the final product. Dust and fibres can be cleanly and efficiently incinerated or gasified for energy applications. And aqueous waste flows can be converted into biogas via fermentation. New generation or 3rd generation biorefineries will be using a mixture of feed stock like agricultural or forest biomass and will produce a multiple products by combining different technologies such a thermochemical and biochemical conversion. This would be zero waste biorefinery, the by-products will be valorised, preferably not by means of utilizing the energy value only. But the feasibility of this is yet to be checked and may be in near future it would be a reality.

4. Conclusion

Conversion of crop residues is essential for sustainable development. Rice straw offers a potential feed stock for the production of bioethanol and several value added products. Utilization of these residues improves the sustainability as well as reduces the negative impacts due to its disposal. Several research and developmental activities were going on in this direction to develop an economically feasible biorefinery concept.

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