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Bioethanol production from rice straw: An overview

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ABSTRACT

Rice straw is an attractive lignocellulosic material for bioethanol production since it is one of the most abundant renewable resources. It has several characteristics, such as high cellulose and hemicelluloses content that can be readily hydrolyzed into fermentable sugars. But there occur several challenges and limitations in the process of converting rice straw to ethanol. The presence of high ash and silica content in rice straw makes it an inferior feedstock for ethanol production. One of the major challenges in developing technology for bioethanol production from rice straw is selection of an appropriate pretreatment technique. The choice of pretreatment methods plays an important role to increase the efficiency of enzymatic saccharification thereby making the whole process economically viable. The present review discusses the available technologies for bioethanol production using rice straw.

1. Introduction

Rice straw is one of the abundant lignocellulosic waste materials in the world. In terms of total production, rice is the third most important grain crop in the world behind wheat and corn. As per FAO statistics, world annual rice production in 2007 was about 650 million tons. Every kilogram of grain harvested is accompanied by production of 1–1.5 kg of the straw (Maiorella, 1985). It gives an estimation of about 650–975 million tons of rice straw produced per year globally and a large part of this is going as cattle feed and rest as waste. The options for the disposition of rice straw are limited by the low bulk density, slow degradation in the soil, harboring of rice stem diseases, and high mineral content. Nowadays, field burning is the major practice for removing rice straw, but it increases the air pollution and consequently affects public health (Mussatto and Roberto, 2004). As climate change is extensively recognized as a threat to development, there is growing interest in alternative uses of agro-industrial residues for energy applications. In this context, rice straw would be a potential candidate for our future energy needs. This review aims to give an overview of the available technologies for bioethanol production using rice straw.

2. Potential of rice straw for fuel ethanol production

Ethanol from biomass has become an increasingly popular alternative to gasoline. However, the production of bioethanol from food crops such as grains (first generation biofuels) has resulted in an undesirable direct competition with food supply. A switch to a more abundant inedible plant material should help to reduce pressure on the food crops. Large parts of these plant materials are made up of complex carbohydrates such as cellulose and hemicelluloses which can be converted to fermentable sugars. Ethanol fermenting microorganisms can utilize these sugars and convert into ethanol.

Rice straw has several characteristics that make it a potential feedstock for fuel ethanol production. It has high cellulose and hemicelluloses content that can be readily hydrolyzed into fermentable sugars. In terms of chemical composition, the straw predominantly contains cellulose (32–47%), hemicellulose (19–27%) and lignin (5–24%) (Garrote et al., 2002; Maiorella, 1983; Saha, 2003; Zamora and Crispin, 1995). The pentoses are dominant in hemicellulose, in which xylose is the most important sugar (14.8–20.2%) (Maiorella, 1983; Roberto et al., 2003). The carbohydrate composition and theoretical ethanol yields of rice straw is shown in Table 1.

The chemical composition of feedstock has a major influence on the efficiency of bioenergy generation. Table 2 lists the chemical properties of rice straw, rice husk, and wheat straw to highlight the particular differences in feedstock. The low feedstock quality of rice straw is primarily determined by a high ash content (10–17%) as compared to wheat straw (around 3%) and also high silica content in ash (SiO_2 is 75% in rice and 55% in wheat) (Zevenhoven, 2000). On the other hand, rice straw as feedstock has the advantage of having a relatively low total alkali content (Na_2O and K_2O typically comprise <15% of total ash), whereas wheat straw can typically have >25% alkali content in ash (Baxter et al., 1996).

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Table 1
Carbohydrate composition and theoretical ethanol yield of rice straw. *Source*: Adapted from Biomass Feedstock Composition and Property Database, Zhu et al. (2005).

Cellulose	38.6%
Hemicellulose	19.7%
Theoretical ethanol yield (L/kg dry)	0.42
Theoretical ethanol yield (gal/MT dry)	110

It is assumed that the hemicellulose fractions are all polymers of xylose.

Table 2
Proximate composition and selected major elements of ash in rice straw, rice husk and wheat straw. *Source*: Jenkins et al. (1998)

	Rice straw	Rice husk	Wheat straw
Proximate analysis (% dry fuel)			
Fixed carbon	15.86	16.22	17.71
Volatile matter	65.47	63.52	75.27
Ash	18.67	20.26	7.02
Elemental composition of ash (%)			
SiO_2	74.67	91.42	55.32
CaO	3.01	3.21	6.14
MgO	1.75	<0.01	1.06
Na_2O	0.96	0.21	1.71
K_2O	12.30	3.71	25.60

Straw quality varies substantially within seasons as well as within regions. If straw is exposed to precipitation in the field, alkali and alkaline compounds are leached, improving the feedstock quality. Thus, the preferred use of this material for bioethanol production is related to both quality and availability.

3. Availability of rice straw

Rice straw is one of the abundant lignocellulosic crop residues in the world. Its annual production is about 731 million tons which is distributed in Africa, Asia, Europe and America (Table 3). This amount of rice straw can potentially produce 205 billion liters bioethanol per year (Balat et al., 2008). In Asia it is a major field-based residue that is produced in large amounts (667.59 million MT). In fact, the total amount equaling 668 million MT could produce theoretically 282 billion liters of ethanol if the technology were available. However, an increasing proportion of this rice straw undergoes field burning. This waste of energy seems inapt, given the high fuel prices and the great demand for reducing greenhouse gas emissions as well as air pollution (Kim and Dale, 2004).

There are primarily two types of residues such as straw and husk from rice cultivation that have potential in terms of energy. Although the technology of using rice husk is well established in many Asian countries, rice straw is rarely used as a source of renewable energy. One of the principal reasons for the preferred use of husk is its easy procurement as it is available at the rice mill. But the collection of rice straw is laborious and its availability is limited to harvest time. The logistics of collection could be improved through baling, but the high cost of equipment makes it uneconomical for most of the rice farmers. Thus, the technologies to use rice straw for the energy purpose must be especially efficient to compensate for the high costs involved in straw collection.

Table 3
Worldwide quantities of rice straw available and theoretical ethanol yield. *Source*: Adapted from Kim and Dale (2004). (Based on the composition of rice straw given in Table 1).

Country	Rice straw availability (million MT)	Theoretical ethanol yield (billion liters)
Africa	20.93	8.83
Asia	667.59	281.72
Europe	3.92	1.65
North America	10.95	4.62
Central America	2.77	1.17
South America	23.51	9.92

4. Production of ethanol from rice straw

4.1. Basic concept

Rice straw consists of three main components, cellulose, hemicellulose and lignin. Technologies for conversion of this feedstock to ethanol have been developed on two platforms, which can be referred to as the sugar platform and the synthesis gas (or syngas) platform. The basic steps of these platforms are shown in Fig. 1. In sugar platform, cellulose and hemicellulose are first converted to fermentable sugars, which then are fermented to produce ethanol. The fermentable sugars include glucose, xylose, arabinose, galactose, and mannose. Hydrolysis of cellulose and hemicellulose to generate these sugars can be carried out by using either acids or enzymes (Drapcho et al., 2008).

In the syngas platform, the biomass is subjected through a process called gasification. In this process, the biomass is heated with no oxygen or only about one-third the oxygen normally required for complete combustion. It subsequently converts to a gaseous product, which contains mostly carbon monoxide and hydrogen. The gas, which is called synthesis gas or syngas, can be fermented by specific microorganisms or converted catalytically to ethanol. In the sugar platform, only the carbohydrate fractions are utilized for ethanol production, whereas in the syngas platform, all three components of the biomass are converted to ethanol (Drapcho et al., 2008).

4.2. Importance of pretreatment

Rice straw is composed of heterogeneous complex of carbohydrate polymers. Cellulose and hemicellulose are densely packed by layers of lignin, which protect them against enzymatic hydrolysis. So it is necessary to have a pretreatment step to break lignin seal to expose cellulose and hemicellulose for enzymatic action. Pretreatment aims to decrease crystallinity of cellulose, increase biomass surface area, remove hemicellulose, and break lignin seal. Pretreatment makes cellulose more accessible to enzymes so that conversion of carbohydrate polymers into fermentable sugars can be achieved more rapidly and with more yields. Pretreatment includes physical, chemical and thermal methods and their combinations. Pretreatment has been viewed as one of the most expensive processing steps in cellulosic biomass-to-fermentable sugars conversion (Mosier et al., 2005).

4.3. Types of pretreatment

4.3.1. Physical pretreatment

Physical pretreatment will increase the accessible surface area and size of pores, and decrease the crystallinity and degrees of polymerization of cellulose. Commonly used physical treatments to degrade lignocellulosic residues include steaming, grinding and milling, irradiation, temperature and pressure.

4.3.1.1. Grinding and milling. Usually grinding and milling are the initial steps of pretreatment of any biomass which reduces the particle size, though the combination of grinding with other pretreatment method has been tried. To an extent it reduces the crystallinity of the biomass. Superfine grinding of steam exploded biomass has been tried and proved better than ground residue

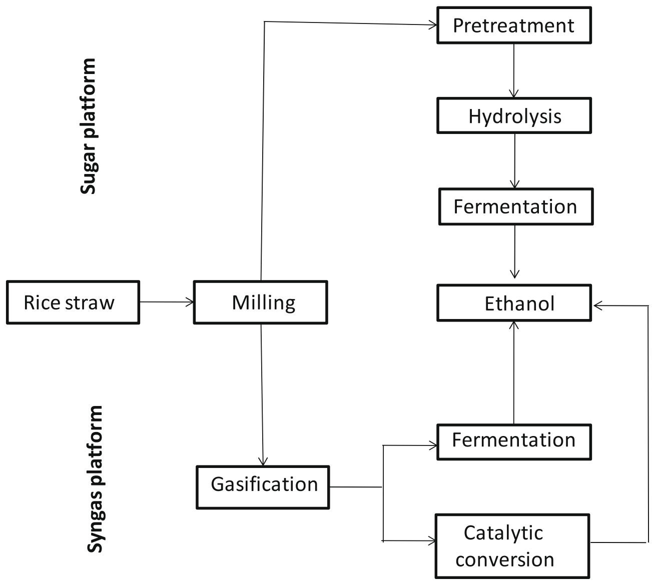

Fig. 1. Basic concept of ethanol production from rice straw.

when hydrolyzed (Jin and Chen, 2006) though energy required for the process also has to be considered while going for commercial applications. For grinding rice straw wet disk milling proved better than ball milling both in terms of glucose recovery as well as energy saving (Hideno et al., 2009). Developments in this field provide a number of pretreatment which permits enzymatic saccharification, e.g. ball milling, roll milling, wet disk milling, and several type of grinding has been tried based on the biomass, though there are no reports particularly on rice straw as such.

4.3.1.2. Electron beam irradiation. The cellulosic fraction of the lignocellulosic materials can be degraded by irradiation to fragile fibers, low molecular weight oligosaccharides and cellobiose (Kumakura and Kaetsu, 1983). It could be due to preferential dissociation of the glucosidal bonds of the cellulose molecular chains by irradiation in the presence of lignin. Irradiation methods are expensive, high energy demanding and have difficulties in industrial application. Jin et al. (2009) carried out physical pretreatment of milled dry rice straw using electron beam irradiation with accelerated electrons by a linear electron accelerator that had the capacity to produce electron beams. Enzymatic hydrolysis of electron beam irradiated and untreated rice straw were carried out and the result indicate that the untreated rice straw produced a glucose yield of 22.6% and the electron beam irradiated sample produced a glucose yield of 52.1% after hydrolysis for 132 h. SEM and X-ray diffraction analysis for the treated rice straw shows physical changes after electron beam irradiation. Because these methods do not involve the use of extreme temperatures, the generation of inhibitory substances produced during acid or alkali pretreatment can be either avoided or minimized.

4.3.1.3. Microwave pretreatment. Microwave irradiation has been widely used in many areas because of its high heating efficiency and easy operation. Microwave irradiation could change the ultra structure of cellulose (Xiong et al., 2000) degrade lignin and hemicelluloses in lignocellulosic materials, and increase the enzymatic susceptibility of lignocellulosic materials (Azuma et al., 1984). Enzymatic hydrolysis of rice straw could be enhanced by microwave pretreatment in presence of water (Azuma et al., 1984; Ooshima et al., 1984) and also in glycerine medium with lesser amount of water (Kitchaiya et al., 2003). Rice straw treated by microwave irradiation alone had almost the same hydrolysis rate and reducing sugar yield compared to the raw straw (Zhu et al., 2005).

4.3.2. Chemical pretreatment

Enzymes cannot effectively convert lignocelluloses to fermentable sugars without chemical pretreatment. The most promising chemicals for pretreatment of rice straw include alkali and ammonia.

4.3.2.1. Alkali pretreatment. Alkali pretreatment involves the application of alkaline solutions like NaOH or KOH to remove lignin and a part of the hemicelluloses, and efficiently increase the accessibility of enzyme to the cellulose. The alkali pretreatment can result in a sharp increase in saccharification yields. Pretreatment can be performed at low temperatures but with a relatively long time and high concentration of the base. Compared with acid or oxidative reagents, alkali treatment appears to be the most effective method in breaking the ester bonds between lignin, hemicellulose and cellulose, and avoiding fragmentation of the hemicellulose polymers (Gaspar et al., 2007).

Alkaline pretreatment of chopped rice straw with 2% NaOH with 20% solid loading at 85 °C for 1 h decreased the lignin by 36% (Zhang and Cai, 2008). The separated and fully exposed microfibrils increased the external surface area and the porosity of the rice straw, thus facilitating enzymatic hydrolysis. The main effect of sodium hydroxide pretreatment on lignocellulosic biomass is delignification by breaking the ester bonds cross-linking lignin and xylan, thus increasing the porosity of biomass (Tarkov and Feist, 1969).

4.3.2.2. Ammonia treatment. As a pretreatment reagent ammonia has number of desirable characteristics. It is an effective swelling reagent for lignocellulosic materials. It has high selectivity for reactions with lignin over those with carbohydrates. Its high volatility makes it easy to recover and reuse. It is a non-polluting and non-corrosive chemical. One of the known reactions of aqueous ammonia with lignin is the cleavage of C–O–C bonds in lignin as well as ether and ester bonds in the lignin–carbohydrate complex (Kim and Lee, 2007).

A flow-through process called Ammonia Recycle Percolation (ARP) was developed for pretreatment. In this process, ammonia is pumped through a bed of biomass maintained at 170 °C. By this process up to 85% delignification and almost theoretical yield of glucose in enzyme hydrolysis can be achieved (Drapcho et al., 2008). Soaking in Aqueous Ammonia (SAA) pretreatment at mild temperatures ranging from 40 to 90 °C for longer reaction times has been used to preserve most of the glucan and xylan in the samples, which is subsequently fermented using the simultaneous saccharification and co-fermentation (SSCF) process (Kim and Lee, 2007; Kim et al., 2008). SAA is still a new method and its effectiveness has not yet been tested for many lignocellulosic feedstock including rice straw. Comparing to other alkalis such as sodium hydroxide or lime, ammonia is highly selective for lignin removal and shows significant swelling effect on lignocellulose. Also, it is easily recoverable due to its high volatility (Wyman et al., 2005). The effectiveness of the SAA process is strongly dependent on the pretreatment temperature.

The ammonia fiber/freeze explosion/expansion (AFEX) process uses anhydrous ammonia instead of aqueous ammonia. Similar to the ARP and SAA process, the ammonia used in the AFEX process can be recovered and recycled due to its high volatility. After treatment, the only exit stream is a gas mix containing ammonia and water vapor. All biomass components remain with the treated solids. Thus, there is no loss of any carbohydrate fraction. Since all of the ammonia will quickly evaporate, there is no need for pH adjustment of the treated material over a wide range before it can be used in subsequent enzyme hydrolysis and ethanol fermentation. Enzyme hydrolysis of AFEX-treated biomass can produce glucose with greater than 90% theoretical yield and xylose with up to 80% theoretical yield. There is no formation of inhibitory compounds (Drapcho et al., 2008). AFEX is reported as an effective pretreatment process for rice straw as it resulted 3% sugar loss during pretreatment (Zhong et al., 2009).

Ferrer et al. (1997) carried out pretreatment of rice straw by a process called Ammonia Pressurization and Depressurization (PDA) using a laboratory-scale ammonia reactor unit consisting of a 4-L reactor with appropriate support equipment. Pretreatment followed by enzymatic hydrolysis resulted significant increase in sugar yield. Ko et al. (2009) carried out aqueous ammonia pretreatment and the optimum conditions were 21% ammonia concentration at 69 °C for 10 h. When AFEX was used in conjunction with 60 FPU of cellulase/g-glucan and β-glucosidase, xylanase and other supplements, the typical glucose yields after 72–168 h of hydrolysis were 60–100% of the theoretical maximum (Murnen et al., 2007).

4.3.2.3. Acid pretreatment. Pretreatment of lignocellulose with acids at ambient temperature enhance the anaerobic digestibility. Dilute acid pretreatment predominantly affect hemicellulose with little impact on lignin degradation. Acid pretreatment will solubilize the hemicellulose, and by this, making the cellulose better accessible to enzymes. Acid pretreatment is usually carried out using mineral acids like HCl and H_2SO_4. Following dilute acid treatment, the enzyme cellulase is needed for hydrolysis of the remaining carbohydrates in the treated biomass. Dilute acid pretreatment can be a simple single-stage process in which biomass is treated with dilute sulfuric acid at suitable acid concentrations and temperatures for a period of time. To reduce enzyme requirements, a two-stage process was developed at the National Renewable Energy Laboratory (NREL) in Golden, Colorado. A schematic diagram of this process is shown in Fig. 2. Literatures regarding dilute acid hydrolysis of rice straw is limited because of the inability of the process to remove lignin and low sugar yield (Sumphanwanich et al., 2008).

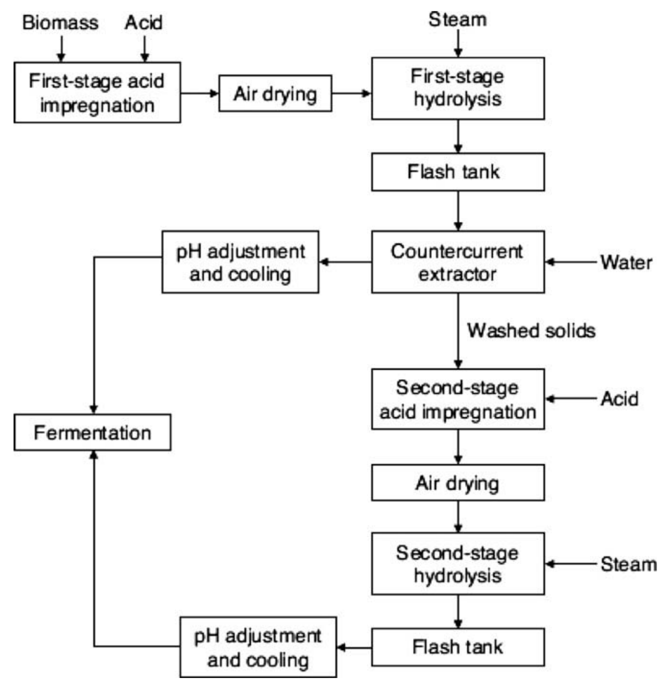

Fig. 2. Schematic flow diagram of the NREL's two-stage dilute sulfuric acid pretreatment process. (*Source*: Drapcho et al. (2008).)

4.3.2.4. Pretreatment with oxidising agent. Oxidative pretreatment involves the addition of an oxidising compound, like hydrogen peroxide or peracetic acid, to the biomass, which is suspended in water. This pretreatment remove the hemicellulose and lignin to increase the accessibility of the cellulose. During oxidative pretreatment several reactions can take place, like electrophilic substitution, displacement of side chains, cleavage of alkyl aryl ether linkages or the oxidative cleavage of aromatic nuclei (Hon and Shiraishi, 2001). Hydrogen peroxide pretreatment utilizes oxidative delignification to detach and solubilize the lignin and loosen the lignocellulosic matrix thus improving enzyme digestibility (Martel and Gould, 1990).

Wei and Cheng (1985) evaluated the effect of hydrogen peroxide pretreatment on the change of the structural features and the enzymatic hydrolysis of rice straw. Changes in the lignin content, weight loss, accessibility for Cadoxen, water-holding capacity, and crystallinity of straw were measured during pretreatment to express the modification of the lignocellulosic structure of straw. The rates and the extents of enzymatic hydrolysis, cellulase adsorption, and cellobiose accumulation in the initial stage of hydrolysis were determined to study the pretreatment effect on hydrolysis. Pretreatment at 60 °C for 5 h in a solution with 1% (w/w) H_2O_2 and NaOH resulted in 60% delignification, 40% weight loss, a fivefold increase in the accessibility for Cadoxen, one times increase in the water-holding capacity and only a slight decrease in crystallinity as compared with that of the untreated straw. Improvement on the pretreatment effect could be made by increasing the initial alkalinity and the pretreatment temperature of hydrogen peroxide solution. A saturated improvement on the structural features was found when the weight ratio of hydrogen peroxide to straw was above 0.25 g H_2O_2/g straw in an alkaline H_2O_2 solution with 1% (w/w) NaOH at 32 °C. The initial rates and extents of hydrolysis, cellulase adsorption, and cellobiose accumulation in hydrolysis were enhanced in accordance with the improved structural features of straw pre-treated. A four times increase in the extent of the enzymatic hydrolysis of straw for 24 h was attributed to the alkaline hydrogen peroxide pretreatment.

Reports are there for employing per acetic acid for the pretreatment of rice straw (Taniguchi et al., 1982; Toyama and Ogawa, 1975). Quantitative changes in the composition of the treated straw, crystallinity of the treated straw and extracted cellulose, and susceptibility of the treated straw with per acetic acid resulted in a slight loss in hemicellulose and cellulose in the straw. The per acetic acid treatments caused little or no breakdown of the crystalline structure of cellulose in the straw. The degree of enzymatic solubilization relative to the amount of residual straw was 42% after treatment with 20% per acetic acid.

4.3.2.5. Organosolv pretreatment. Organosolv pretreatment enhances the enzymatic digestibility mainly by delignification and hemicellulose removal leaving a cellulose-rich residue, which can be hydrolyzed with enzymes at high rates and to almost theoretical glucose yield. Hemicellulose and lignin can be recovered for production of high-value co-products. The change of cellulose crystallinity during organosolv pretreatment is not clear yet, but it has been found that the swelling of cellulose in organic solvent strongly depends on the species of organic solvents, solvent concentration and temperature (Mantanis et al., 1994, 1995). The organosolv process uses hot organic solvents such as ethanol at acidic pH to fractionate biomass components. It was first considered for paper making, but recently it has also been considered for pretreatment of lignocellulosic feedstock for ethanol production. There are some inherent drawbacks to the organosolvent pretreatment. Organosolvent pretreatment is expensive at present than the leading pretreatment processes but the separation and recycling of the applied solvent could reduce the operational costs of the process. It also requires strict controlled conditions due to the volatility of organic solvents. Removal of solvents from the pre-treated cellulose is usually necessary because the solvents might inhibit enzymatic hydrolysis and fermentation or digestion of hydrolysate (Xuebing et al., 2009). The commonly used organic solvents for pretreatment are solvents with low boiling points like ethanol and methanol and alcohols with high boiling points like ethylene glycol, glycerol, tetrahydrofurfuryl alcohol and other organic compounds like dimethylsulfoxide, ethers, ketone, and phenols (Thring et al., 1990). Organosolv processes, if the pretreatment is conducted at high temperatures (185–210 °C), there is no need for acid addition but at lower temperature requires addition of catalysts (Sun and Cheng, 2002).

Jamshid et al. (2005) reported rice straw pulping using diethylene glycol, mixture of diethylene glycol and ethylene glycol at atmospheric pressure. Pretreatment with high boiling point solvents enhance delignification. The most important advantage for high boiling point alcohol pretreatment is that the process can be performed under atmospheric pressure. Jahan (2006) reported acetic acid or formic acid pretreatment of rice straw with the variation of reaction variables. Maximum pentosan dissolution was observed in 80% acetic acid with 0.6% H_2SO_4 catalyst at 80 °C for 120 min. Acetic acid dissolved pentosan more slowly than formic acid.

4.3.3. Biological pretreatment

Biological pretreatment offers some conceptually important advantages such as low chemical and energy use, but a controllable and sufficiently rapid system has not yet been found. Chemical pretreatments have serious disadvantages in terms of the requirement for specialized corrosion resistant equipment, extensive washing, and proper disposal of chemical wastes. Biological pretreatment is a safe and environmentally-friendly method for lignin removal from lignocellulose. The most promising microorganisms for biological pretreatment are white-rot fungi that belong to class Basidiomycetes (Taniguchi et al., 2005).

The effects of biological pretreatment of rice straw using four white-rot fungi (*Phanerochaete chrysosporium*, *Trametes versicolor*, *Ceriporiopsis subvermispora*, and *Pleurotus ostreatus*) were evaluated on the basis of quantitative and structural changes in the components of the pre-treated rice straw as well as susceptibility to enzymatic hydrolysis (Taniguchi et al., 2005). Of these white-rot fungi, *P. ostreatus* selectively degraded the lignin fraction of rice straw rather than the holocellulose component. When rice straw was pre-treated with *P. ostreatus* for 60 d, the total weight loss and the degree of Klason lignin degraded were 25% and 41%, respectively. After the pretreatment, the residual amounts of cellulose and hemicellulose were 83% and 52% of those in untreated rice straw, respectively. By enzymatic hydrolysis with a commercial cellulase preparation for 48 h, 52% holocellulose and 44% cellulose in the pre-treated rice straw were solubilized. The net sugar yields based on the amounts of holocellulose and cellulose of untreated rice straw were 33% for total soluble sugar from holocellulose and 32% for glucose from cellulose (Taniguchi et al., 2005). The biological pretreatment induces structural loosening of cells with a simultaneous increase in porosity. The Scanning Electron Microscopic (SEM) observations show that the pretreatment with *P. ostreatus* resulted in an increase in susceptibility of rice straw to enzymatic hydrolysis due to partial degradation of the lignin that is responsible for preventing penetration of cellulase in the rice straw as described above.

Patel et al. (2007) did a preliminary study on the microbial pretreatment and fermentation of the agricultural residues like rice straw. A combination of five different fungi viz. *Aspergillus niger, Aspergillus awamori, Trichoderma reesei, Phenerochaete chrysosporium, Pleurotus sajor-caju*, obtained from screening were used for pretreatment and *Saccharomyces cereviseae* (NCIM 3095) was used for carrying out fermentation. Pretreatment with *A. niger* and *A. awamori* and later fermentation yielded highest amount of ethanol ($2.2\ g\ L^{-1}$).

4.3.4. Combined pretreatment

Kun et al. (2009) reported pretreatment of rice straw with alkali assisted by photocatalysis which efficiently changed the physical properties and microstructure of rice straw also resulted in decrease in lignin content and thereby increasing the enzymatic hydrolysis rate of the pre-treated rice straw had. Alkali treatment of rice straw in the absence of H_2O_2 favored solubilization of the small molecular size of hemicelluloses, which are rich in glucose, probably originating from α-glucan, while the second stage treatment by alkaline peroxide enhanced dissolution of larger molecular size hemicelluloses, which were rich in xylose (Sun et al., 2000). Microwave is emerging as an important and efficient pretreatment method when applied in combination with other methods. Zhu et al. (2006) reported several combinations of microwave pretreatment of rice straw along with acid and alkali which removes hemicellulose and lignin, respectively, and microwave removes more lignin compared to pretreatment with alkali alone. The results show that higher microwave power with shorter pretreatment time and the lower microwave power with longer pretreatment time had almost the same effect on the weight loss and composition at the same energy consumption. Microwave enhances some reactions in the pretreatment, but the detailed mechanism is still unclear.

Lu and Minoru (1993) reported radiation pretreatment of rice straw in the presence of NaOH solutions using an electron beam accelerator. Electron beam irradiation alter lignocellulosic structure so that NaOH solution could enter easily into the lignocellulosic complex and increase the rate of reaction so the lignin will be eliminated more easily and cellulose or hemicellulose scissored by irradiation was degraded slightly by NaOH which in turn increase the enzyme accessibility.

Jin and Chen (2006) studied a combination of steam explosion and superfine grinding of rice straw and its enzymatic hydrolysis. Superfine grinding were combined with low severity steam explosion for treating rice straw to shorten the grinding time, save the energy cost, avoid the inhibitors, and obtain high enzymatic hydrolysis. Superfine grinding was conducted after rice straw was steam exploded at low R_o (steam explosion severity factor) to avoid excessive decomposition of hemicellulose and side products generation from sugars and lignin. It shows difference in enzymatic hydrolysis, chemical compositions, fiber characteristics and composed cells contents of the superfine ground steam exploded rice straw product and the ground steam exploded rice straw residue. Enzymatic hydrolysis of the superfine ground product gained the highest hydrolytic rate and yielded more reducing sugar, while the reducing sugar yield generated from the superfine ground residue was even lower than that from the untreated rice straw. Steam explosion and super fine grinding decrease particle size and improve reactive surface to the largest content, and it had been considered to be no more energy consuming than traditional mechanical grinding with respect to the increase of surface area.

4.4. Enzymatic hydrolysis

Enzymatic hydrolysis is the second step in the production of ethanol from lignocellulosic materials. It involves cleaving the polymers of cellulose and hemicellulose using enzymes. The cellulose usually contains only glucans, whereas hemicellulose contains polymers of several sugars such as mannan, xylan, glucan, galactan, and arabinan. Consequently, the main hydrolysis product of cellulose is glucose, whereas the hemicellulose gives rise to several pentoses and hexoses (Taherzadeh and Niklasson, 2004). However, high lignin content blocks enzyme accessibility, causes end-product inhibition, and reduces the rate and yield of hydrolysis. In addition to lignin, cellobiose and glucose also act as strong inhibitors of cellulases (Knauf and Moniruzzaman, 2004).

Various factors influencing the yields of the lignocellulose to the monomeric sugars and the by-products are, e.g., particle size, liquid to solid ratio, type and concentration of acid used, temperature, and reaction time, as well as the length of the macromolecules, degree of polymerization of cellulose, configuration of the cellulose chain, association of cellulose with other protective polymeric structures within the plant cell wall such as lignin, pectin, hemicellulose, proteins, and mineral elements.

Recent advances in enzyme technology for the conversion of cellulosic biomass to sugars have brought significant progress in lignocellulosic ethanol research. Enzymatic hydrolysis is usually carried out under mild conditions, i.e., low pressure and long retention time in connection to the hydrolysis of hemicellulose. Valdes and Planes (1983) studied the hydrolysis of rice straw using 5–10% H_2SO_4 at 80–100 °C. They reported the best sugar yield at 100 °C with 10% H_2SO_4 for 240 min. Yin et al. (1982) studied the hydrolysis of hemicellulose fraction of rice straw with 2% H_2SO_4 at 110–120 °C, where they succeeded to hydrolyze more than 70% of pentoses. Valkanas et al. (1998) carried out hydrolysis of rice straw with different acids with varying concentrations (0.5–1% H_2SO_4, 2–3% HCl and 0.5–1% H_3PO_4) and they found that after 3 h retention time, rice straw pentosans converted to a solution of monosaccharides, suitable for fermentation. Roberto et al. (2003) studied the effects of H_2SO_4 concentration and retention time on the production of sugars and the by-products from rice straw at relatively low temperature (121 °C) and long time (10–30 min) in a 350-L batch reactor. The optimum acid concentration of 1% and retention time of 27 min was found to attain high yield of xylose (77%). The pretreatment of the straw with dilute sulfuric acid resulted in 0.72 g g^{-1} sugar yield during 48 h enzymatic hydrolysis, which was higher than steam-pretreated (0.60 g g^{-1}) and untreated straw (0.46 g g^{-1}) (Abedinifar et al., 2009). When they increased the concentration of substrate from 20 to 50 and 100 g L^{-1} sugar yield lowered to 13% and 16%, respectively.

The kinetics of glucose production from rice straw by *Aspergillus niger* was studied by Aderemi et al. (2008). Glucose yield was found to increase from 43 to 87% as the rice straw particle size decreased from 425 to 75 μm, while the optimal temperature and pH were found within the range of 45–50 °C and 4.5–5, respectively. The study shows that the concentration and rate of glucose production is depend on pretreatment of rice straw, substrate concentration and cell loading. Enzymatic hydrolysis of alkali assisted photocatalysis of rice straw resulted 2.56 times higher hydrolysis rate than that of alkali process (Kun et al., 2009) whereas, ammonia treated rice straw resulted an increase of monomeric sugars from 11% in the untreated to 61% (Sulbaran-de-Ferrer et al., 2003). Hydrolysis efficiency of lignocellulosic biomass increases when combination of enzymes such as cellulase, xylanases and pectinases are employed rather than only cellulase (Zhong et al., 2009) but the cost of the process increases drastically even though from ecological point of view it is highly desirable.

4.5. Fermentation

The cellulose and hemicellulose fraction of rice straw can be converted to ethanol by either simultaneous saccharification and fermentation (SSF) or separate enzymatic hydrolysis and fermentation (SHF) processes. SSF is more favored because of its low potential costs (Wyman, 1994). It results in higher yield of ethanol compared to SHF by minimizing product inhibition. One of the drawbacks of this process is the difference in optimum temperature of the hydrolyzing enzymes and fermenting microorganisms. Most of the reports states that the optimum temperature for enzymatic hydrolysis is at 40–50 °C, while the microorganisms with good ethanol productivity and yield do not usually tolerate this high temperature. This problem can be avoided by applying thermo-tolerant microorganisms such as *Kluyveromyces marxianus*, *Candida lusitaniae*, and *Zymomonas mobilis* or mixed culture of some microorganisms like *Brettanomyces clausenii* and *Saccharomyces cerevisiae* (Golias et al., 2002; Spindler et al., 1988).

Punnapayak and Emert (1986) studied SSF of alkali-pre-treated rice straw with *Pachysolen tannophilus* and *Candida brassicae*, where *P. tannophilus* resulted in higher ethanol yields than *C. brassicae* in all the experiment. However, they achieved only less than 30% of theoretical ethanol yield. SSF of acid-pre-treated rice straw with *Mucor indicus*, *Rhizopus oryzae*, and *S. cerevisiae* resulted an overall yield of 40–74% of the maximum theoretical ethanol yield (Karimi et al., 2006). The SSF of alkali and microwave/alkali pretreated rice straws to ethanol using cellulase from *T. reesei* and *S. cerevisiae* were studied by Zhu et al. (2006). Under the optimum conditions ethanol concentration reached 29.1 g L^{-1} and ethanol yield was 61.3%. The study shows that production of ethanol from microwave/alkali pre-treated rice straw had lower enzyme loading, shorter reaction time, and achieved higher ethanol concentration and yield than rice straw pre-treated by alkali alone. There are many reports stating that the simultaneous saccharification and fermentation (SSF) is superior to the traditional saccharification and subsequent fermentation in the production of ethanol from rice straw because the SSF process can improve ethanol yields by removing end-product inhibition of saccharification process and eliminate the need for separate reactors for saccharification and fermentation (Chadha et al., 1995).

Separate enzymatic hydrolysis and fermentation of rice straw by *M. indicus*, *R. oryzae*, and *S. cerevisiae* were studied by Abedinifar et al. (2009). Their study concludes that *M. indicus* is able to produce ethanol from pentoses. This species seems to be a good strain for production of ethanol from lignocelluloses, particularly for rice straw.

In addition to SSF and SHF, there is another process called consolidated bioprocessing (CBP). In this process, cellulase production, biomass hydrolysis, and ethanol fermentation are carried out together in a single reactor. A microorganism that can efficiently ferment cellulose directly to ethanol, such as *Clostridium phytofermentans*, will be most suitable for this process.

Glucose and xylose are two dominating sugars in the lignocellulosic hydrolysates. The main difficulty of using two microorganisms for the co-fermentation of these two sugars is the inability to provide optimal environmental conditions for the two strains simultaneously (Chandrakant and Bisaria, 1998). A majority of previous studies on strain co-cultures reported that, while the fermentation of glucose in the sugar mixture proceeded efficiently with a traditional glucose-fermenting strain, the fermentation of xylose was often slow and of low efficiency due to the conflicting oxygen requirements between the two strains and/or the catabolite repression on the xylose assimilation caused by the glucose (Grootjen et al., 1991; Kordowska-wiater and Targonski, 2002). Approaches in both process engineering and strain engineering have been carried out to circumvent these difficulties and to improve the system efficiency. Examples of process engineering include continuous culture (Grootjen et al., 1991; Laplace et al., 1993; Delgenes et al., 1996), the immobilization of one of the strains (Grootjen et al., 1991), co-immobilization of two strains (Grootjen et al., 1991; deBari et al., 2004), two stage fermentation in one bioreactor (i.e. sequential culture) (Fu and Peiris, 2008), and separate fermentation in two bioreactors (Taniguchi et al., 1997; Grootjen et al., 1991).

5. Conclusions

The utilization of lignocellulosic biomass for bioethanol production necessitates the production technology to be cost-effective and environmentally sustainable. Considering the evolution and need of second generation biofuels, rice straw appears a promising and potent candidate for production of bioethanol due to its abundant availability and attractive composition. Biological conversion of rice straw into fermentable sugars, employing hydrolyzing enzymes is at present the most attractive alternative due to environmental concerns. Though there are several hindrances on the way of developing economically feasible technology due to its complex nature, high lignin and ash content, several work is going onto develop an efficient pretreatment method to remove unwanted portion so as to get readily available sugars and considerable success has been achieved till date. The available statistics shows that the need of bioethanol for transport sector could be met by using rice straw. Approaches in both process engineering and strain engineering still have to be carried out to circumvent the difficulties of xylose and glucose co-fermentation and to improve the system efficiency. A very balanced and intelligent combination of pretreatment, hydrolysis and fermentation process has to be selected for maximum efficacy of the process. With the advent of genetically modified yeast, synthetic hydrolysing enzymes, other sophisticated technologies and their efficient combination, the process of bioethanol production employing rice straw will prove to be a feasible technology in very near future.

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