International Journal of Biology, Pharmacy and Allied Sciences (IJBPAS)

'A Bridge Between Laboratory and Reader'

www.ijbpas.com

PRODUCTION OF BIO-ETHANOL FROM RICE HUSK: EFFECT USING DIFFERENT PRE-TREATMENTS AND FERMENTATION INHIBITORS: A REVIEW

PANCHAL B AND SHRIVASTAV A[*]

Department of Microbiology, Parul Institute of Applied Sciences, Parul University, Vadodara, 391760, Gujarat, India

*Corresponding Author: E Mail: anupama.shrivastav82045@paruluniversity.ac.in

ABSTRACT

Rice is staple food and the byproduct of husk which is rich in cellulose, can be converted into Bio-ethanol production. Rice husk is one of the lignocelluloses feed stocks in the world. It contains mixture of pentose and hexose sugars. It is selected for ethanol production. Rice husk is also major byproduct of rice milling. Rice husk is the important biomass byproduct of the rice. An industry produces 20% of the total cereal production and is considered as a waste. Bio-ethanol is an environmental alternative to petroleum energy sources. Bio-ethanol produced by lignocellulosic waste such as rice husk can be most economical and efficient. Lignocellulosic material is an important feedstock for Bio-ethanol production because of increasing environmental and food security concerns. The production of bio-ethanol from lignocellulosic waste comes under the second generation bio-fuel production. The use of agricultural residual wastes is the cost effective way for the ethanol production.

INTRODUCTION

Bio-ethanol production is the agricultural wastes due to food and feed competition [4]. The use of the agricultural residual wastes is the cost effective for the production of bio-ethanol. Rice is the third most important grain crop around the world. As per food and

agriculture organization, the world yearly rice production in 2007 was 650 million tons. Accordingly it's estimated that the 650-975 million tons of rice straw produced every year all around world **[60]**. Large part of rice, residual waste is made up of complex carbohydrates like cellulose and hemicelluloses. Cellulose and hemicelluloses can be converted into sugars and ethanol

fermenting microorganisms can utilize the sugars convert into ethanol. Chemical composition for rice straw consists of cellulose (32-47%), hemicelluloses (19-27%) and lignin (5-24%) [60] Composition of rice husk it contains 75-90% of organic matter such as lignin, cellulose and hemicelluloses **[75]**.
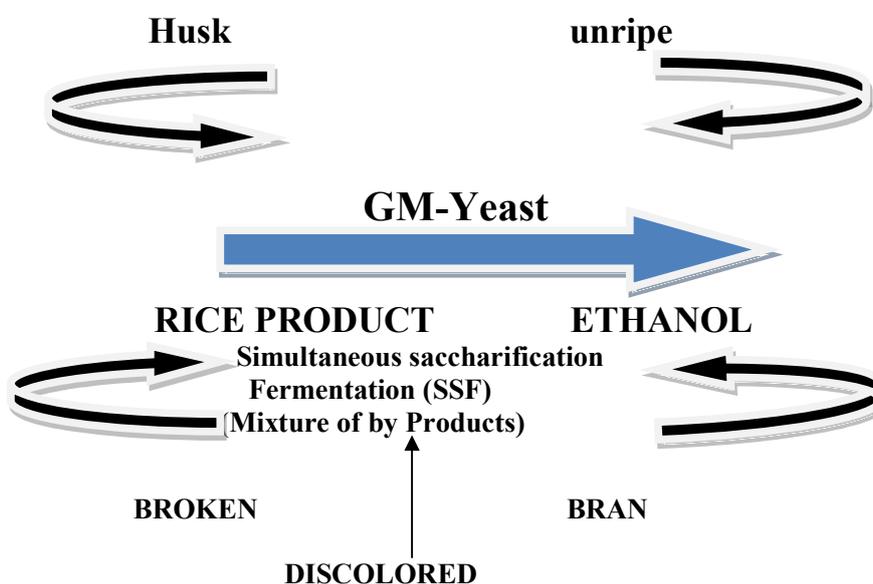

Figure 1: Production of bio-ethanol from different waste

Rice husk generally contains approximately 29.3% hemicelluloses and approximately 34.4% cellulose which can be degraded to get reducing sugars **[13]**. Rice straw is one of the most important lignocellulosic materials which is easily found anywhere around the world. Its yearly production is about 73 million tons globally produce a huge amount of bio-ethanol per year. The worldwide

yearly rice husk out is about 80 million tons with an annual energy potential of 1.2×10^9 GJ, corresponding to a heating value of 15 MJ/kg **[85]**. The technology of using rice husk is usually in trend in Asia whereas the rice straw is rarely used as the renewable resource in industries. The reason for this is that rice husk is easily available at the rice mills at any time throughout the year whereas

the availability of rice straw is limited to harvest time. Rice husk constitutes about one fifth of the annual gross rice production of the world [2]. The production of ethanol from lignocellulosic waste comes under the second generation bio-fuel production. It is an alternative to the first generation bio-fuels which are produced directly from the food crops such as sugarcane, potatoes, corn etc. and emerges into the food and fodder concerns [10]. This residual waste contains cellulose, hemicelluloses and lignin. Several pretreatment techniques are required to remove hard outer covering. Bio-fuel has the potential to reduce greenhouse gas emissions produced from the vehicles; since atmospheric carbon dioxide is removed through renewable biomass feed stocks during biomass growth. Bio-ethanol is a renewable bio-fuel which can be used as a valuable alternative for gasoline or a suitable blend for it. Although corn has a limited capacity for ethanol production, it has been known as the primary feedstock for the production of commercial ethanol. Bio-ethanol production with the use of lignocellulosic biomass (LB) is most promising as an alternative for the traditional starch feedstock [38]. The lignocellulosic biomass formed by three structural polymers: cellulose, hemicelluloses, lignin, and small quantities of other compounds. Lignocellulosic biomass contain five major sugars such as glucose, mannose, galactose, xylose, and arabinose. All sugars, glucose, the major unit of cellulose, are the first most abundant sugar in lignocellulosic biomass. There are numerous lignocellulosic agricultural wastes available for bio-ethanol production, which included sugarcane bagasse, rice husk, willow, switch grass, softwood, rice straw, wheat straw and etc. [70]. Rice husk (RH), the outer cover of rice grain, which accounts for about 20% w/w of rice, has the potential to produce approximately 0.4 g sugars per 1 g of dry rice husk, and further process sugars can be fermented into bio-ethanol [49]. It's widely available at a low cost and relatively high ethanol production makes rice husk a favorable raw material for the future of ethanol production. For increasing carbon conversion efficiency the rice husk need pretreatment in order to remove lignin, reduce cellulose crystallinity, increases porosity, and release the monomeric sugars that can be fermented to bio-ethanol [6]. Pretreatment is one of the most expensive and crucial step-in the process of bio-ethanol production. An effective pretreatment must be economical, minimize sugar loss, maximize lignin removal, and limit inhibitor

formation which includes furfurals and acetic acid. Various pretreatments such as alkaline [6], lime [71], microwave alkali [70], acid [19, 6], dilute acid [36], alkaline peroxide [72], microwave [83], Hot-compressed water [62], ultrasonic and H2O2 [91], biological [63], ionic liquid pretreatment [65], and air oxidation [7] pretreatment have been tested on rice husk. However, these systems (in the case of acid or alkaline methods) include some drawbacks such as high cost of neutralizing, corrosion problems, and implications in reusability [42]. Ammonium carbonate ($(NH_4)_2CO_3$), can be a promising solvent in pretreatment, and a substitute for ammonia, since they both have a weak base. This pretreatment, which could be applied to CO_2 capture system, has the advantage of being employed as a continuous and massive treatment system [43] have employed this on rice straw pretreatment, they have found that ammonium carbonate pretreatment increased the external surface area and removed the amorphous fraction of rice straw, result in enhanced enzymatic digestibility. Several strategies for the bio-ethanol production may be applied at the fermentation stage, such as separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), and semi-simultaneous saccharification and fermentation (SSSF), the

main advantages of SSF process are comparatively lower costs, higher ethanol yields due to removal of feedback inhibition on enzymatic saccharification and reduction in the required number of vessels or reactors compared to SHF [44]. However, the difference between the optimal temperatures is an issue for the enzyme action and microorganism growth for an efficient SSF [74]. Because of the novelty and effectively of ammonium carbon-ate pretreatment method. Rice husk was first pretreated by ammonium carbonate solution at 80°C. Next is the glucan digestibility yield of the pretreated RH was conducted with the use of commercial cellulase enzyme. Third is the ethanol yield was investigated in SSF process using active *Saccharomyces cerevisiae* yeast. The substrates before and after pretreatment are characterized and compared with analytical methods. Briefly, the scanning electron microscopy (SEM) was applied to map the substrate morphological changes and Fourier Transform infrared spectroscopy (FTIR) were used to characterize the chemical compositional and physical structural changes. The issues of global warming and the depleting oil reserves throughout the world is allow to discovery of the resources which could be renewable and be utilized as a feedstock for the production

of bio-ethanol, an alternative energy resource for the crude oil. Due to the increasing pressure for the crude oils, there is a huge necessity for the finding of an alternative energy or a suitable blend for it [52]. The benefit of the bio-ethanol using lignocelluloses agro wastes (LCAWs) as a feedstock with respect to that of the fossil fuel is that it reduces the greenhouse gas resource. Bio-ethanol becomes the renewable fuel possessing the probability of replacing the crude oils because of its positive net energy balance and life cycle is compatible instead of being competitive with the world food and feed production chains [61]. Due to the renewability and inexpensive availability of the LCAWs, these are the propitious renewable resources for the production of bio-ethanol. Utilization of the LCAWs which are non-food sources for the production of bio-fuels becomes the alternative source of energy. they are cheap, unutilized and locally available most of the times [1]. They are appraised to be a better source for the production of bio-ethanol. they are composed of a large amount of polysaccharide which can be fragmented to produce fermentable sugars. Every year, LCAWs husks, seeds and whole pomace are generated which can initiate a form of dissipating which are left on the land or inadequately degraded. They

are chemically made up of cellulose (35–50%), hemicelluloses (25–35%) and lignin (10–15%) with the insignificant amount of ash [88]. LCAWs for the production of bio-ethanol rely on the bio-conversion of cellulose, hemicellulose and lignin. The lignin have a polyphenolic complex mainly composed of p-coumaryl, sinapyl and coniferyl alcohols, hydroxyphenyl and syringyl units [53]. Which limit the bioconversion of the cellulose and hemicellulose to reducing sugars by enzymatic hydrolysis and finally to ethanol [32]. Hence the process of conversion of the LCAWs to ethanol is becoming a difficult process [80]. The production of bio-ethanol utilizing the LCAWs involves treatment such as pre-treatment, enzymatic hydrolysis and fermentation. The pre-treatment process is considered for the transformation of carbohydrate of bio-residues to simple sugars. Several pretreatment methods for delignification have been reported using alkali [35], acid pretreatment [78] and microwave pretreatment [54]. These pretreatments hydrolyze lignin and make the cellulose and hemicellulose easily available for the hydrolytic enzymes to produce fermentable sugars. Moreover, by the pretreatment methods, some of the inhibitors are produced [54] such as acetic acid, formic

acid, furfural and 5-hydroxymethylfurfural (HMF) which are considered as the inhibitors of fermentation of ethanol [55]. Furthermore, an additional step for the detoxification of the inhibitors formed during the pretreatment of biomass. A satisfactory detoxification consequence can be reached by the combination of two or more methods [31]. However, pretreatment methods to detoxify the hydrolysates add cost weight. the LCAWs steam pretreated which require a very low amount of energy in contrast to the mechanical where 70% of higher energy is required for size reduction by the conventional methods as compared with steam pretreatment [57]. Bio-ethanol production in India is basically from the sugarcane molasses and sweet sorghum which are of high industrial demand and blending them with petrol is not feasible and hence, bio-ethanol production should incorporate more crops and forestry residues [1]. LCAWs via; corn husk, coffee cherry husk and peanut husk are available abundantly in local crop fields were burnt or left as such. The saccharified hydrolysate of LCAW was further fermentation by Saccharomyces cerevisiae, Candida tropicalis and also with their co-culture to bio-ethanol. The purpose of coculture is the utilization of both hexose and pentose for this process is

the ethanol tolerance by pentose fermenting yeasts [25]. Production of bio-ethanol using for various pretreated LCAWs. saccharification of LCAWs which is the main step for the maximum production of ethanol. Bio-ethanol is derived from corn grains (starch) and sugarcane (sucrose) and these are for fertile land as well as food production. The food crops are modified to improve yield at very short periods, in the future, utilization of these food sources for ethanol production will further complicate the already existing food and energy in human population continue to increase [16]. Therefore, utilization of lignocellulosic biomass is an attractive feedstock for future supplies of ethanol considering its great availability, low cost and non-competition with human food sources [37]. Economic and environmental concerns are the major propelling factors that have made the search for alternatives to fossil fuels a subject of intensive research; demands for these alternative sources continue to increase and lignocellulosic plant biomass have been identified as promising renewable Feedstock for bio-fuel production [30]. Lignocellulosic biomass from plants is cheap and readily available. the cellulose and hemicelluloses components of lignocellulosic biomass can be efficiently converted to ethanol

considering the large amounts of glucose monomers present in them [34]. In Nigeria, rice is widely cultivated principally for its grains and its husks are abundantly available as waste and in few areas used as feeds for ruminant. Rice husk is little economic use presently; therefore, it used as suitable lignocellulosic substrate for bio-ethanol production. Cellulose is the most important source of glucose, and is found in lignocellulosic biomass and wastes including agricultural residues such as forestry residues and pulping wastes, cereal straws, and threshing husks, as well as food processing coproduces such as brewers spent grain [29, 64] reported in 1990, there were about 2900 million tons of lignocellulosic waste from cereal crops, 160 million tons from pulse crops, 14 million tons from oilseed crops and 540 million tons from plantation crops. Rice is the most widely grown cereal crops an abundance of rice husk and rice straw lignocellulosic wastes [93]. The world annual production of rice husk has been reported as approximately 120 million tons [5, 41] reported that 667.59 million tons rice straw were at that time produced in Asia, and Binod and colleagues [8] calculated that this could theoretically be converted into 281.72 billion liters of ethanol. Which hampers the hydrolysis of the polysaccharides to

fermentable monosaccharide [46] generally, four important steps: hydrothermal pre-treatment, enzymatic or chemical saccharification, fermentation and purification. The aim of pre-treatment is to separate the lignin from the cellulose, reduce cellulosic crystalline and improve the accessibility of cellulose to celluloses [11]. The fermentable sugars released can be latterly converted to products by microorganisms such as bacteria and yeasts [12]. Finally, the product can be recovered from the fermentation liquor, for example by distillation. Each of all steps has a range of options, and the different combinations of four steps can cause various results. lignocellulosic ethanol process includes: efficient pretreatment methods of lignocelluloses, availability of low cost hydrolytic enzymes, and use of optimal microbial strains is capable of converting hexose and pentose sugar to ethanol at high rated yield, and final concentrations [15]. Rice husk is agricultural waste, accounting for about one fifth of the annual gross rice, 545 million metric tons, of the world [5]. Rice husk predominantly contains hemicellulose and cellulose and these can be hydrolyzed into sugars at approximately 0.426 g of sugars per 1 g of dry rice husk [49]. With further process the sugars can be

fermented into ethanol at about 0.21 g of ethanol per 1 g of dry rice husk [17]. The pre-treatment is necessary to making carbohydrates for enzymatic hydrolysis and fermentation [50]. The biological conversion of lignocellulosic biomass to ethanol is to release of the cellulose portion (and subsequently glucose) from the lignocellulosic structure [21]. Pretreatment includes physical, chemical, biological and thermal methods and their combinations. High temperature acid treatments are hydrolyzing cellulose to yield sugars. This process in formation of degradation products like 5-hydroxymethyl furfural which will interfere microbial fermentation [50]. Alkali pretreatment is a typical chemical pretreatment method and a combination of microwave irradiation with alkali may be an alternative pretreatment approach for lignocellulosic materials at lower temperature to solve the pretreatment problem [68, 69]. The cellulose component from the pretreatment process can be converted to ethanol in a two-step process where the cellulose is first converted to glucose sugars by hydrolysis; then after sugars can in turn converted to ethanol by fermentation [67]. Cellulose is mixture of three different enzymes: first is endoglucanase, which attacks regions of low

crystalline in the cellulose fiber, creating free chain-ends; second is exoglucanase or third one is cellulobiohydrolase, Which are further degrade by removing cellobiose unit from the free chain-ends; and beta-glycosidase, Which hydrolyzes cellobiose to produce glucose, in much smaller amounts [27]. The most widely used cellulase from *Trichoderma reesei* is poor in cellobiase, and thus re strict the conversion of cellobiose to glucose [67]. The accumulation of cellobiose will cause severe feedback inhibition to the cellulase reaction [23]. Therefore, cellulose complex system is crucial to increase enzymatic hydrolysis yield. Glucose and xylose are the two prevailing sugars in lignocellulosic hydrolyzates after saccharification. Both need to be fermented efficiently, but current approaches are inefficient, since no native microorganisms can convert all sugars into ethanol at high yield [68, 69]. Enzymatic hydrolysis of alkali pretreated rice husk biomass by crude enzymes produced by *Aspergillus heteromophus*. Enzymatic hydrolyzes fermented by *Saccharomyces cerevisiae*, *Scheffersomyces stipitis* and their co-culture for bio-ethanol production.

Importance of pretreatment

Rice straw is heterogenous complex composed of carbohydrate polymers. Cellulose and hemicelluloses are packed by

layers of lignin, which protect against enzymatic hydrolysis. It's necessary pre-treatment step to break lignin seal to expose cellulose and hemicelluloses for enzymatic action. Pre-treatment is used to decrease crystalline of cellulose and increase biomass surface area it also remove hemicelluloses and break lignin seal. Pretreatment make cellulose more accessible to enzymes so the conversion of carbohydrate polymers into fermentable sugars can be achieved more rapidly and with more yields. Pre-treatment include also physical, chemical and thermal methods and their combinations. Pre-treatments one of the most expensive process in cellulosic biomass conservation of fermentable sugar [50].

Physical pretreatment

Physical pretreatment increase the accessible surface area and size of pores, and decrease the crystalline and degree of polymerization of cellulose. Commonly this method used for physical treatments to degrade lignocelluloses residues includes steaming, grinding and milling, irradiation, temperature and pressure.

Chemical pretreatment

Enzymes can't effective to convert lignocelluloses to fermentable sugars without chemical pre-treatment. The chemicals pre-

treatment of rice straw include alkali and ammonia.

Alkali pretreatment

Alkali pre-treatment involves the application of alkaline solutions like NaOH or KOH to remove lignin and a part of the hemicelluloses and increase the accessibility of enzyme to the cellulose. Pretreatment can be performed at low temperatures but with a long time and high concentration of the base. This is compared with acid and oxidative reagents. Alkali treatment is the most effective method for breaking the ester bonds between lignin, hemicelluloses, cellulose, and avoiding fragmentation of the hemicelluloses polymers [26]. Alkaline pre-treatment of rice straw with 2% NaOH and 20% solid, is loading at 85 degree Celsius for 1 hour it's decreased the lignin by 36% [92]. The separated and unguarded micro fibrils increased on external surface area hereby facilitating enzymatic hydrolysis. The main effect of sodium hydroxide pre-treatment on lignocellulosic biomass is delignification by breaking ester bonds cross-linking lignin and xylan, it's increasing the porosity of biomass [79].

Ammonia treatment

Ammonia pretreatment reagent ammonia has number of desirable characteristics. It is an effective reagent for lignocellulosic

materials. It is a non-polluting and noncorrosive chemical. One of the known reaction 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 [39]. A flow through process is called Ammonia Recycle Percolation (ARP) it's developed for pre-treatment. In this process, ammonia is pumped through a bed of biomass maintained at 170 degree Celsius. By this process up to 85% delignification and yield of glucose in enzyme hydrolysis can be achieved [20]. Soaking in Aqueous Ammonia (SAA) pretreatment at mild temperatures ranging from 40 to 90 degree Celsius for longer reaction times has been used to preserve most of the glucan and xylan in the sample, which is subsequently, fermented using the simultaneous saccharification and co-fermentation (SSCF) process [39]. Soaking in Aqueous Ammonia (SAA) is 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 effect on lignocellulose. Also it is easily recoverable due to its high volatility [84]. The SAA process is dependent on the pretreatment temperature. The ammonia fiber/explosion/expansion (AFEX) process uses for the anhydrous ammonia instead of aqueous ammonia. Similar to the ammonia recycle percolation and soaking in aqueous ammonia process, the ammonia used in the AFEX process it can be recovered and recycled due to its high volatility. After treatment the only exit steam is a gas mix containing ammonia and water vapor. All biomass components exist with the treated solids all of the ammonia will quickly evaporate, there is no need for pH adjustment of the treated material before it can be used in subsequent enzyme hydrolysis and ethanol fermentation. Enzyme hydrolysis of Aqueous Fiber/Explosion/expansion is treated biomass can produce glucose with greater than 90% yield and xylose with up to 80% yield. There is no production of inhibitory compounds [20]. Aqueous fiber/explosion/expansion is reported as an effective pretreatment process for rice straw as it resulted 3% sugar loss during pretreatment. [94] Carried out pretreatment of rice straw a process called Ammonia Pressurization and Depressurization (PDA). PDA using lab-scale ammonia reactor unit consisting of 4-Litre with appropriate equipment. Pretreatment followed by enzymatic hydrolysis is increase in sugar yield [45]

carried out aqueous ammonia pretreatment and the optimum conditions were 21% ammonia concentration at 69 degree Celsius for 10 hour. When Aqueous Fiber/Explosion/expansion was used in conjunction with 60 FPU of cellulose/glucan, b-glucosidase, xylanase and other supplements. The glucose yields after 72–168 hour of hydrolysis were 60–100% of maximum yield [58].

Acid pretreatment

Acid Pretreatment of lignocellulose with acids at temperature enhances the anaerobic digestibility. Dilute acid pretreatment affect on hemicellulose with little impact on lignin degradation. Acid pretreatment will solubilize hemicellulose, and by this, making the cellulose better accessible to enzymes. Acid pre-treatment used mineral Acids such as HCl and H_2SO_4. Dilute acid treatment, the enzyme cellulase is needed for hydrolysis of the remaining carbohydrates in the treated biomass. Dilute acid pre-treatment 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. Diluted acid hydrolysis of rice straw is limited because of the inability of the process to remove lignin and low sugar yield [77].

Analytical method

Different analytical methods were used to determine whether the degradation of sample has done and further for the qualitative changes in the sample. The estimation of ethanol yield done by gas chromatography. Total reducing sugar in enzymatic hydrolyses was estimated by DNS method [51]. The enzymatic hydrolyses was concentrated by the methods of Dehkhoda *et al*. [18]. The estimation of ethanol was done by Spectrophotometer [14].

Fermentation

Concentrated enzymatic hydrolyses of different sugar concentration was use for ethanol production. The hydrolyses was inoculated with 2% v/v of a 48 h old seed culture of *S. cerevisiae, Pichia stipitis* and co-culture (1:1) of both yeast. Incubation was carried out in Stoppard flasks at room temperature (28 ± 2 degree Celsius) without agitation. Sample were withdrawn after 36 hour (optimized fermentation time) [67], centrifuged for 10 min at 4 ˚C at 10,000 rpm and supernatant analyzed for ethanol and residual reducing sugar contents.

Ethanol obtained from fermentation media

Yeast (*S. cerevisiae*) has been historically used for second generation bio-ethanol production because of its fermentative capacity and ethanol tolerance. The rice husk being non-edible and of low economic profile makes the utilization of the plant part of advantage in ethanol production. The yields of ethanol from FeCl3 and NaOH pretreatments methods showed that these pretreatment methods on rice husk did not produce substances which were capable of inhibiting the yeast cells from converting the reducing sugars to ethanol; as $FeCl_3$ treated sample were observed to have yield the highest amount of reducing sugars compared to other treatments. Analysis of the fermentation broth after fermentation indicates that most of the initially present reducing sugars converted to ethanol via fermentation unlike the water treated samples which still have much reducing sugars left (0.270 ± 0.018 and 0.232 ± 0.048 mg/ml for separate hydrolysis and fermentation and simultaneous saccharification and fermentation, respectively) after fermentation. The inhibition of enzymatic activities in the water treated fermenting media of direct inhibition of catabolic enzymes, generation of reactive oxygen species, decreased intracellular pH, ATP depletion and toxic anion accumulation. The ethanol produced from water pretreatment was the lowest. However, its yield was comparable to that of the HCl treatment. Water treatment could be advantageous to the industry as no additional chemicals are required costly materials that are resistant to corrosion for the scale-up.

Simultaneous saccharification and fermentations (SSF)

Simultaneous Saccharification and Fermentation was carried out at a low temperature (25 °C) by simultaneously adding cellulose (Ctec-2) and a yeast strain (*Saccharomyces cerevisiae NCYC 2826*) which ferment hexose sugars, but not pentoses **[82]**. Four pretreatment severities spanning the range used above were selected from low to very high. Bio-ethanol yield higher from rice straw compared with Rise husk after pre-treatment, indicating that yeast behave different on the different lignocelluloses hydrolyses. Bio-ethanol yield were very low in both Rice husk and Rice straw pre-treated, which suggest that yeast behavior was being suppressed **[82]** and washing pre-treated. In Rice straw simultaneous saccharification and fermentation (SSF) reduced in and that's due to the removal of fermentation inhibitors. The impact of inhibitors appears to be predominantly on the fermentation.

Chemical analysis of supernatants from pre-treated rice husk and rice straw by using nuclear magnetic resonance (NMR)

A range of breakdown and solubilized components during pre-treatment of the rice husk and rice straw is analyzing by the liquors by Nuclear Magnetic Resonance. The 25 different compounds were readily detectable and quantifiable. The diagnostic spectral regions of the compounds for rice husk and rice straw samples pre-treated. The quantities of this compounds as affected by severity of pre-treatment. The components identified and categorized as: unidentified compounds, seven sugars and established fermentation inhibitors. The compounds released during low severity pre-treatments. Several organic acids typically found in intermediary metabolism such as pyruvic acid, succinic acid, fumaric acid and 2-oxoglutaric acids. In addition, acetone, glycolic acid and glycerol were detected. Succinate acid, fumarate acid and pyruvate acid were produced in higher quantities at higher severities, and particularly in pre-treated rice straw. Ethanol was produced in small quantities from both pre-treated rice husk (PTRH) and pre-treated rice straw (PTRS). Betaine levels and trends differed between PTRH and PTRS, showing degradation at higher severities in PTRH.

Generally, rice husk released higher amounts of sugar compounds more than rice straw. The presence of galactose may reflect the hydrolysis of small quantities of peptic polymers in the cereal biomass while the xylose, xylo-oligomers and arabinose are likely to be derived from xylans and arabinoxylan hemicelluloses Compounds to cause significant inhibition on saccharification or fermentation released [81]. Most of the inhibitors increase with increasing severities. Hydroxyl-methyl furfural (5-HMF), furfural (2-FA) and acetic acid were the most abundant inhibitors produced from both pre-treated rice husk and pre-treated rice straw. [81] reported higher levels of all the inhibitors were produced from rice husk, consistent with the higher levels of sugar release and break down. The levels of 5-HMF, 2-FA and acetic acid produced at the much higher severities were very much greater [81] (Confirmed by HPLC). This due to two factors: firstly by the maximum pre-treatment severity, while the severity went to higher levels. Secondly it is very likely considerable quantities of volatile compounds were lost into the steam during the explosion process. The amount of formic acid, acetol, acetaldehyde and methanol produced from pre-treated samples. Choline acid and levulinic acid also produced lower

level than the other inhibitors and produced more from pre-treated rice straw less than pre-treated rice husk.

CONCLUSION

Rice husk and rice straw are important sources of biomass for bio-refining. The acidic treatment is better compared to alkaline treatment in lignin content. the ethanol yield obtained after SSF is maximum at 2% H_2SO_4 in acidic pretreated samples and 3% NaOH in alkali pretreated samples. Bio-ethanol produced by lignocelluloses waste such as rice husk. It's most economical and efficient. It is produced under optimum condition and strategies. SSF is an effective way of production of bio-ethanol

ACKNOWLEDGEMENT

REFERENCES

[1] Arora, S. Priya, P. Sharma, S. Sharma, L. Nain, Evaluating biological pretreatment as a feasible methodology for ethanol production from paddy straw, Biocatal. Agric. Biotechnol. (2016).

[2] Abba, S. Ansumal, *Bioenerg. Res.*, **2010**, 3, 328-334.

[3] Abbas A, Ansumali S. Global potential of rice husk as a renewable feedstock for ethanol biofuel production. Bioenergy Res. 2010; 3(4):328–34.

[4] A.B. Rabah, S.B. Oyeleke S.B. Manga, L.H. Gusao, *IJESD.*, **2014**, 5.

[5] Abbas A, Ansumali S. Global Potential of Rice husk as a renewable feedstock for ethanol biofuel production. Bioenerg Res 2010; 3: 328–34.

[6] Ang, T.N., Ngoh, G.C., Chua, A.S.M., 2013. Comparative study of variouspretreatment reagents on rice husk and structural changes assessment of theoptimized pretreated rice husk. Bioresour. Technol. 135, 116–119.

[7] Banerjee, S., Sen, R., Pandey, R.A., Chakrabarti, T., Satpute, D., Giri, B.S., Mudliar, S., 2009. Evaluation of wet air oxidation as a pretreatment strategy for bioethanolproduction from rice husk and process optimization. Biomass Bioenergy 33, 1680–1686.

[8] Binod P, Sindhu R, Singhania RR, Vikram S, Devi L, Nagalakshmi S,

Kurien N, Sukumaran RK, Pandey A. Bioethanol production from rice straw: an overview. Bioresour Technol. 2010; 101(13): 4767–74.

[9] Brett CT, Waldron KW. Physiology and biochemistry of plant cell walls .Berlin: Springer Science and Business Media; 1996.

[10] B.K. Ahring, M. Alapuranen, A. Berlin, R. Bura, R.P. Chandra, J. Cherry, J.P. VanDijken, M. Galbe, *Biofuel. Adv. Biochem. Eng.*, **2007**, 3.

[11] Cheng JJ, Stomp AM. Growing duckweed to recover nutrients from wastewaters and for production of fuel ethanol and animal feed. Clean Soil Air Water. 2009; 37(1): 17–26.

[12] Carlozzi P, Buccioni A, Minieri S, Pushparaj B, Piccardi R, Ena A, Pintucci C. Production of bio-fuels (hydrogen and lipids) through a photofermentation process. Bioresour Technol. 2010; 101(9): 3115–20.

[13] C.S. Kumar, R. Mythily, S. Chandraju, *J. Chem. Pharm. Res.*, **2012**, 4, 3588-3591.

[14] Caputi AJ, Ueda M, Brown T. Spectrophotometric determination

of ethanol in wine. Am. J. Enol. Vitti. 1968; 19: 160–5.

[15] Chen Y. Development and application of co-culture for ethanol production by co-fermentation of glucose and xylose: a systematic review. J Ind Microbiol Biotechnol 2011; 38: 581–97.

[16] De Fraiture C, Giordano M, Liao Y (2008) Biofuels and implications for agricultural water use: blue impacts of green energy. Water Policy 10 (Supplement 1): 67–81.

[17] Demirbas A. Bioethanol from cellulosic materials: a renewable motor fuel from biomass. Energy Sour 2005; 2005(27): 327–37.

[18] Dehkhoda A, Tomas B, Taherzadeh MJ. Comparison of vacuum and high pressure evaporated wood hydrolyzate for ethanol production by repeated fedbatch using flocculating *Saccharomyces cerevisiae*. BioResources 2008; 4(1): 309–20.

[19] Dagnino, E.P., Chamorro, E.R., Romano, S.D., Felissia, F.E., Area, M.C., 2013.Optimization of the acid pretreatment of rice hulls to obtain fermentable sugars for bioethanol

production. Ind. Crops Prod. 42, 363–368.

[20] Drapcho, C.M., Nhuan, N.P., Walker, T.H., 2008. Biofuels Engineering Process Technology. Mc Graw Hill Companies, Inc.

[21] El-Zawawy WK, Ibrahima MM, Abdel-Fattahb YR, Soliman NA, Mahmoud MM. Acid and enzyme hydrolysis to convert pretreated lignocellulosic materials into glucose for ethanol production. Carbohyd Polym 2011; 84: 865–71.

[22] E.P. Dagnino, E.R. Chamorro, S.D. Romano, F.E. Felissia, M.C. Area, Optimization of the acid pretreatment of rice hulls to obtain fermentable sugars for bioethanol production, Ind. Crops Prod. 42 (2013) 363–368.

[23] Fang H, Zhao C, Song XY. Optimization of enzymatic hydrolysis of steam exploded corn stover by two approaches: Response surface methodology or using cellulase from mixed cultures of Trichoderma reesei RUT-C30 and Aspergillus niger NL02. Bioresour Technol 2010; 101: 4111–9.

[24] Ferrer, S. *et al.*, 1997. Sugar production from rice straw. Arch. Latinoam. Prod. Anim.5, 112–114.

[25] F. Latif, M.I. Rajoka, Production of ethanol and xylitol from corn cobs by yeasts, Bioresour. Technol. 77 (2001) 57–63.

[26] Gaspar, M., Kalman, G., Reczey, K., 2007. Corn fibre as a raw material for hemicellulose and ethanol production. Process Biochem. 42, 1135–1139.

[27] Gottschalk LMF, Oliveira RO, Bon EPS. Cellulases, xylanases, b-glucosidase and ferulic acid esterase produced by *Trichoderma* and *Aspergillus* act synergistically in the hydrolysis of sugarcane bagasse. Biochem Eng J 2010; 51: 72–8.

[28] Gray KA, Zhao L, Emptage M (2006) Bioethanol. Curr Opin Chem Biol 10: 141–146.

[29] Hasunuma T, Okazaki F, Okai N, Hara KY, Ishii J, Kondo A. A review of enzymes and microbes for lignocellulosic biorefinery and the possibility of their application to consolidated bioprocessing technology. Bioresour. Technol. 2013; 135: 513–22.

[30] Hannon M, Gimpel J, Tran M, Rasala B, Mayfield S (2010) Biofuels from algae: challenges and potential. Biofuels 1(5): 763–784.

[31] H. Chen, W. Qiu, Key technologies for bioethanol production from lignocellulose, Biotechnol. Adv. 28 (2010) 556–562.

[32] H. Jørgensen, J.B. Kristensen, C. Felby, Enzymatic conversion of lignocellulose into fermentable sugars: challenges and opportunities, Biofuels Bioprod. Bioref. (2007) 119–134.

[33] H. Zhang, N. Li, X. Pan, S. Wu, J. Xie, Oxidative conversion of glucose to gluconic acid by iron (III) chloride in water under mild conditions, Green Chem. (2016).

[34] Ibeto CN, Ofoefule AU, Agbo KE (2011) A global overview of biomass potentials for bioethanol production: a renewable alternative fuel. Trends Appl Sci Res., 6: 410–425.

[35] J.K. Ko, E. Ximenes, Y. Kim, M.R. Ladisch, Adsorption of enzyme onto lignins of liquid hot water pretreated hardwoods, Biotechnol. Bioeng. 9999 (2014): 1–11.

[36] Imamoglu, E., Sukan, F.V., 2013. Scale-up and kinetic modeling for bioethanol production. Bioresour. Technol. 144, 311–320.

[37] Kim S, Dale BE. Global potential bio-ethanol production from wasted crops and crop residues. Biomass Bioenergy. 2004; 26 (4): 361–75.

[38] Kim, T.H., Kim, T.H., 2014. Overview of technical barriers and implementation of cellulosic ethanol in the U.S. Energy, 66, 13–19.

[39] Kim, T.H., Lee, Y.Y., 2007. Pretreatment of corn stover by soaking in aqueous ammonia at moderate temperatures. Appl. Biochem. Biotechnol., 81–92.

[40] Kumar P, Barrett DM, Delwiche MJ, Stroeve P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Ind Eng Chem Res. 2009; 48(8):3713–29.

[41] Kim S, Dale BE (2004) Global potential bioethanol production from wasted crops and crop residue. Biomass Bioenergy 26:361–375.

[42] Karimi, K., Emtiazi, G., Taherzadeh, M.J., 2006. Ethanol production from dilute-acid pretreated rice straw by

simultaneous saccharification and fermentation with *Mucor indicus, Rhizopus oryzae, and Saccharomyces cerevisiae.* EnzymeMicrob. Technol. 40, 138–144.

[43] Kim, I., Lee, B., Song, D., Han, J.I., 2014. Effects of ammonium carbonate pretreatment on the enzymatic digestibility and structural features of rice straw. Bioresour. Technol. 166, 353–357. http://dx.doi.org/10.1016/j.biortech. 2014.04.101.

[44] Karimi, K., Emtiazi, G., Taherzadeh, M.J., 2006. EnzymeMicrob. Technol. 40, 138–144, http://dx.doi.org/10.1016/j.enzmicte c.2005.10.046.

[45] Ko, J.K., Bak, J.S., Jung, M.W., Lee, H.J., Choi, I.-G., Kim, T.H., Kim, K.H., 2009. Ethanol production from rice straw using optimized aqueous-ammonia soaking pretreatment and simultaneous saccharification and fermentation processes. Bioresour. Technol. 100, 4374–4380.

[46] Lattanzio V, Lattanzio VM, Cardinali A. Role of phenolics in the resistance mechanisms of plants against fungal pathogens and insects. Phytochem Adv Res. 2006; 661: 23–67.

[47] Lin L, Yan R, Liu Y, Jiang W. In-depth investigation of enzymatic hydrolysis of biomass wastes based on three major components: cellulose, hemicelluloses and lignin. Bioresour. Technol. 2010; 101(21): 8217–23.

[48] L. da Costa Sousa, M. Jina, S. Chundawat, V. Bokade, X. Tang, A. Azarpira, F. Lu, U. Avci, J. Humpula, N. Uppugundla, C. Gunawan, S. Pattathil, A. Cheh, N. Kothari, R. Kumar, J. Ralph, G.M. Hahn, E.C. Wyman, S. Singh, A.B. Simmons, E. Bruce, E.B. Dale, V. Balan, Next-generation ammonia pretreatment enhances biofuel production from biomass via simultaneous cellulose decrystallization and lignin extraction, Energy Environ. Sci. (2015), https://doi.org/10.1039/x0xx00000x.

[49] Megawati, Sediawan WB, Sulistyo H, Hidayat M. Kinetics of sequential reaction of hydrolysis and sugar degradation of rice husk in ethanol

production: Effect of catalyst concentration. Bioresour Technol 2011; 102: 2062–7.

[50] Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, *et al.* Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour Technol 2005; 96: 673–86.

[51] Miller GL. Use of dinitrosalicylic acid reagent for determination of reducing sugar. Anal Chem 1959; 31: 426–8.

[52] M. Ebrahimi, O.B. Villaflores, E.E. Ordono, A.R. Caparanga, Effects of acidified aqueous glycerol and glycerol carbonate pretreatment of rice husk on the enzymatic digestibility , structural characteristics , and bioethanol production, Bioresour. Technol. 228 (2018) 264–271.

[53] M. Wojtusik, C.J. Villar, M. Zuritaa, M. Ladero, Study of the enzymatic activity inhibition on the saccharificaation of acid pretreated corn stover, Biomass Bioenergy 98 (2017) 1–7.

[54] M.J. Wang, Y.F. Huang, P.T. Chiueh, W.H. Kuan, S.L. Lo, Microwave-induced to rarefaction of

rice husk and sugarcane residues, Energy 37 (2012): 177–184 https://doi.org/10.1002/hlca.200490 224.

[55] M.H.B. Klinke, Inhibition of ethanol-producing yeast and bacteria by degradation products produced during pre-treatment of biomass, Appl. Microbiol. Biotechnol. (2004) 10–26 https://doi.org/10.1007/s00253-004-1642-2.

[56] M. Jin, C. Sousa, C. Schwartz, Y. He, C. Sarks, C. Gunawan, V. Balan, B.E. Dale,Towards lower cost cellulosic biofuel production using ammonia based pretreatment technologies †, Green Chem. (2015), https://doi.org/10.1039/c5gc02433a.

[57] M.T. Holtzapple, Energy requirements for the size reduction of poplar and aspen wood, Biotechnol. Bioeng. 33 (1989) 207–210.

[58] Murnen, H.K., Balan, V., Chundawat, S.P.S., Bals, B., Sousa, L.D.C., Dale, B.E., 2007. Optimization of ammonia fiber expansion (AFEX) pretreatment and enzymatic hydrolysis of Miscanthus

_ giganteus to fermentable sugars. Biotechnol. Prog. 23, 846–850.

[59] Nuwamanya E, Chiwona-Karltun L, Kawuki RS, Baguma Y. Bio-ethanol production from non- food parts of cassava (Manihot esculenta Crantz). Ambio. 2012; 41(3): 262–70.

[60] P. Binod, R. Sindhu, R.R. Singhania, S. Vikram, L. Devi, S. Nagalakhshmi, N. kurein, R.K. Sukamaran, A. Pandey, *Bioresour. Technol.*, **2009**, 101, 4767-4774.

[61] P.V. Neves, A.P. Pitarelo, L.P. Ramos, Production of cellulosic ethanol from sugarcane bagasse by steam explosion : effect of extractives content , acid catalysis and different fermentation technologies, Bioresour. Technol. 208(2016): 184–194 https://doi.org/10.1016/j.biortech.20 16.02.085.

[62] Phaiboonsilpa, N., Ogura, M., Yamauchi, K., Rabemanolontsoa, H., Saka, S., 2013.Two-step hydrolysis of rice (Oryza sativa) husk as treated by semi-flowhot-compressed water. Ind. Crops Prod. 49, 484–491, http://dx.doi.org/10.1016/j.indcrop.2 013.05.025.

[63] Potumarthi, R., Baadhe, R.R., Nayak, P., Jetty, A., 2013. Simultaneous pretreatmentand sacchariffication of rice husk by Phanerochete chrysosporium for improved production of reducing sugars. Bioresour. Technol. 128, 113 117,http://dx.doi.org/10.1016/j.biort ech.2012.10.030.

[64] Rajaram S, Varma A. Production and characterization of xylanase from *Bacillus thermo alkalophilus* grown on agricultural wastes. Appl Microbiol Biotechnol. 1990; 34(1): 141–4.

[65] Salanti, A., Zoia, L., Frigerio, P., Orlandi, M., 2013. Influence of acidic and alkaline aqueous regeneration on enzymatic digestibility of the cellulose fraction recovered from Cl-treated rice husk. Bioresour. Technol. 128, 330 336,http://dx.doi.org/10.1016/j.biort ech.2012.10.057.

[66] Singh A, Bishnoi NR. Enzymatic hydrolysis optimization of microwave alkali pretreated wheat straw and ethanol production by yeast. Bioresour. Technol

2011.http://dx.doi.org/10.1016/j.bior tech.2011.12.084.

[67] Singh A, Bishnoi NR. Optimization of Ethanol production from microwave alkali pretreated rice straw using statistical experimental designs by Saccharomyces cerevisiae. Ind Crops Prod 2012.http://dx.doi.org/10.1016/ j.indcrop.2011.12.033.

[68] Singh A, Nigam PS, Murphy JD. Renewable fuels from algae: an answer to debatable land based fuels. Bioresour Technol. 2011; 102(1):10–6.

[69] Singh A, Tuteja S, Singh N, Bishnoi NR. Enhanced saccharification of rice straw and hulls by microwave-alkali pretreatment and lignocellulolytic enzyme production. Bioresour Technol.2011; 102: 1773–82.

[70] Singh, R., Shukla, A., 2014. A review on methods of flue gas cleaning from combustion of biomass. Renew. Sustain. Energy. Rev. 29, 854–864, http://dx.doi.org/10.1016/j.rser.2013 .09.005

[71] Saha, B.C., Cotta, M.A., 2008. Lime pretreatment, enzymatic saccharification and fermentation of rice hulls to ethanol. Biomass Bioenergy 32, 971–977, http://dx.doi.org/10.1016/j.biombioe .2008.01.014.

[72] Saha, B.C., Cotta, M.A., 2007. Enzymatic saccharification and fermentation of alkaline peroxide pretreated rice hulls to ethanol. Enzyme Microb. Technol. 41,528– 532, http://dx.doi.org/10.1016/j.enzmicte c.2007.04.006.

[73] Singh, A., Bajar, S., Bishnoi, N.R., 2014. Enzymatic hydrolysis of microwave alkali pretreated rice husk for ethanol production by *Saccharomyces cerevisiae, Scheffersomyces stipitis* and their co-culture. Fuel 116, 699–702, http://dx.doi.org/10.1016/j.fuel.2013 .08.072

[74] Sarkar, N., Ghosh, S.K., Bannerjee, S., Aikat, K., 2012. Bioethanol production from agricultural wastes: an overview. Renew. Energ. 37, 19– 27, http://dx.doi.org/10.1016/j.renene.20 11.06.045.

[75] S. Kumar, P. Sangwan, R. Dhankhar, V. Mor, S. Bidra, *Res. J. Chem. Env. Sci*., **2013**, 1, 126-129.

[76] S. Vijayalaxmi, K.A.A. Appaiah, S.K. Jayalakshmi, V.H. Mulimani, K. Sreeramulu, Production of bioethanol from fermented sugars of sugarcane bagasse produced by lignocellulolytic enzymes of *exiguobacterium sp* . VSG-1, Appl. Biochem. Biotechnol. (2013), https://doi.org/10.1007/s12010-013-0366-0.

[77] Sumphanwanich, J., Leepipatpiboon, N., Srinorakutara, T., Akaracharanya, A., 2008. Evaluation of dilute-acid pretreated bagasse, corn cob and rice straw for ethanol fermentation by *Saccharomyces cerevisiae*. Ann. Microbiol. 58, 219–225.

[78] T.N. Ang, G.C. Ngoh, A. Seak, M. Chua, Comparative study of various pretreatmentreagents on rice husk and structural changes assessment of the optimized pretreated rice husk, Bioresour. Technol. 135 (2013) 116–119 https://doi.org/10.1016/j.biortech.2012.09.045.

[79] Tarkov, H., Feist, W.C., 1969. A mechanism for improving the digestibility of materials with dilute alkali and liquid ammonia. Adv. Chem. Ser. 95, 197–218.

[80] V. Menon, M. Rao, Trends in bioconversion of lignocellulose: biofuels , platform chemicals & biorefinery concept, Prog. Energy Combust. Sci. 38 (2012): 522–550 https://doi.org/10.1016/j.pecs.2012.02.002.

[81] Wood IP, Cao H-G, Tran L, Cook N, Ryden P, Wilson DR, Moates GK, Collins SRA, Elliston A, Waldron KW. Comparison of saccharification and fermentation of steam exploded rice straw and rice husk. Biotechnol Biofuels. 2016; 9(1): 193.

[82] Wu J, Elliston A, Le Gall G, Colquhoun IJ, Collins SRA, Dicks J, Roberts IN, Waldron KW. Yeast diversity in relation to the production of fuels and chemicals. Sci Rep. 2017;7(1):14259.

[83] Wang, M.J., Huang, Y.F., Chiueh, P.T., Kuan, W.H., Lo, S.L., 2012. Microwave-induced torrefaction of rice husk and sugarcane residues. Energy 37, 177–184, http://dx.doi.org/10.1016/j.energy.2011.11.053.

[84] Wyman, C.E., Dale, B.E., Elander, R.T., Holtzapple, M., Ladisch, M.R., Lee, Y.Y., 2005. Coordinated development of leading biomass pretreatment technologies. Bioresour. Technol. 96, 1959–1966.

[85] X.Z. Yuan, Y. Liu, H.J. Huang, H. Wang, G.M. Zeng, X.L. Wang, *Fuel. Process. Technol.*, **2013**, 112, 93-99.

[86] X. Wang, Y.F. Tsang, Y. Li, X. Ma, S. Cui, T.A. Zhang, J. Hu, M.T. Gao, Inhibitory effects of phenolic compounds of rice straw formed by saccharification during ethanol fermentation by *Pichia stipitis*, Bioresour. Technol. 244 (2017) 1059–1067

[87] https://doi.org/10.1016/j.biortech.20 17.08.096.

[88] Y.R. Loh, D. Sujan, M.E. Rahman, C.A. Das, Resources, Conservation and Recycling Sugarcane bagasse — the future composite material : a literature review, Resour. Conserv. Recycl. 75 (2013) 14–22 https://doi.org/10.1016/j.resconrec.2 013.03. 002.

[89] Y. Zhang, X. Fu, H. Chen, Pretreatment based on two-step steam explosion combined with an

intermediate separation of fiber cells-Optimization of fermentation of corn straw hydrolysates, Bioresour. Technol. 121 (2012) 100–104 https://doi.org/ 10.1016/j.biortech.2012.07.006.

[90] Yang, B., Wyman, C.E., 2008. Pretreatment: the key to unlocking low-cost cellulosicethanol. Biofuels. Bioprod. Biorefining 2, 26–40, http://dx.doi.org/10.1002/bbb.49.

[91] Yu, J., Zhang, J., He, J., Liu, Z., Yu, Z., 2009. Combinations of mild physical or chemical pretreatment with biological pretreatment for enzymatic hydrolysis of rice husk. Bioresour. Technol. 100, 903–908, http://dx.doi.org/10.1016/j.biortech. 2008.07.025.

[92] Zhang, Q.Z., Cai, W.M., 2008. Enzymatic hydrolysis of alkali-pretreated rice straw by *Trichoderma reesei* ZM4-F3. Biomass Bioenergy 32, 1130–1135.

[93] Zhang DQ, Tan SK, Gersberg RM. Municipal solid waste management in China: status, problems and challenges. J Environ Manag. 2010; 91(8): 1623–33.

[94] Zhong, C., Lau, M.W., Balan, V., Dale, B.E., Yuan, Y.J., 2009.

Optimization of enzymatic hydrolysis and ethanol fermentation from AFEX-treated rice straw. Appl. Microbiol. Biotechnol. 84, 667–676.

[95] Zhao, Y. Cao, Z. Ma, Q. Shao, Optimization of liquid ammonia pre-treatment conditions for maximizing sugar release from gaint reed (*Arundo donax* L.), Biomass Bioenergy 98 (2017) 61–69.