Enhanced biogas production from rice straw with various pretreatment : a review

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Abstrack - *Rice straw is one of organic material that can be used for sustainable production of bioenergy and biofuels such as biogas (about 50-75% CH_4 and 25-50% CO_2). Out of all bioconversion technologies for biogas production, anaerobic digestion (AD) is a most cost-effective bioconversion technology that has been implemented worldwide for commercial production of electricity, heat, and compressed natural gas (CNG) from organic materials. However, the utilization of rice straw for biogas production via anaerobic digestion has not been widely adopted because the complicated structure of the plant cell wall makes it resistant to microbial attack. Pretreatment of recalcitrant rice straw is essential to achieve high biogas yield in the AD process. A number of different pretreatment techniques involving using physical pretreatment (hydrothermal and freeze), chemical pretreatment (sodium carbonate – sodium sulfite, hydrogen peroxide, NMMO, alkaline, and dilute acid) and biological pretreatment (fungal pretreatment) also combined pretretment (microwave irradiation and chemical) approaches have been investigated, but there is no report that systematically compares the performance of these pretreatment methods for application on rice straw for biogas production. This paper reviews the methods that have been studied for pretreatment of rice straw for delignification, reducing sugar, and conversion to biogas. It describes the AD process, structural and compositional properties of rice straw, and various pretreatment techniques, including the pretreatment process, parameters, performance, and advantages vs. drawbacks.*

Keywords : Biogas, Rice straw, Pretreatment, Methane

1. INTRODUCTION

Since the beginning of the industrial revolution, the required energy for the developed industries has been extremely increased all around the world [1]. However, ease of access to the fossil fuels during almost two centuries has decreased the available fossil fuel reservoirs, causing the rising prices. Therefore, the energy supply for the future has become one of the most important global problems [2]. On the other hand, combustion of fossil energy carriers like petrol, natural gas and coal has led to the release of CO_2, NOx and SOx, which all cause huge environmental problems and adverse effects on human health and ecosystem [3].

Agriculture is not only important from the economic point of view but even agricultural waste such as wheat straw, rice straw, can play an important role in meeting the growing energy demand of the society in a sustainable manner. In particular, lignocellulosic agricultural crops waste has huge unutilized energy generation potential [4]. Rice ranked at third as major agricultural crop grown in the world, in term of total cultivated area of 161.42

million hectare with a gross grain yield production of 678.69 million tonnes in year 2009. The total estimated dry lignocellulosic biomass production from rice cultivation stood at about 905 million tonnes per annum [5]. The pretreatment of lignocellulosic biomass offers higher biodegradation rate and overall main product yield in any biological energy conversion processes [6]. As the matter of fact that the most part of biomass contents (carbohydrates, fats and proteins) in anaerobic digestion process are converted into simple derivatives, which finally transforms into biogas (CH4+CO2) with the help of different types of anaerobic micro-organisms [4]. Further again, it has been found that biogas-to-electricity is among technologies having increasing production potential on criteria-based evaluation of low carbon power technologies. Therefore, biogas is able to contribute carbon neutral electricity. Moreover, by applying carbon capture and sequestration into biogas-to-electricity the negative net CO_2 emissions can be achieved [7].

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Anaerobic digestion (AD) of agricultural residues and other biodegradable wastes is widely used as the best treatment options because it yields methane and CO_2 rich biogas which is suitable for energy production [8,9]. Anaerobic digestion of organic waste and residues, therefore, combines both sustainable treatment and renewable energy production [10,11]. AD generally involves four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. At the beginning of the process, hydrolysis occurs as extracellular enzymes, which are produced by hydrolytic microbes, decompose complex organic polymers to simple soluble monomers. Proteins, lipids, and carbohydrates are hydrolyzed to amino acids, long-chain fatty acids, and sugars, respectively. These small molecules are then converted by fermentative bacteria (acidogens) to a mixture of volatile fatty acids (VFAs) and other minor products such as alcohol. Acetogenic bacteria further convert the VFAs to acetate, carbon dioxide, and/or hydrogen, which provide direct substrates for methanogenesis, the last step of the AD process for methane production [12].

The degradation of lignocelluloses into biogas is a complicated process, since lignocelluloses have a recalcitrant structure which is naturally designed to prevent enzymatic degradation. Lignocelluloses are formed in a compact and crystalline structure and often contain a high amount of lignin. In order to permit degradation of these materials in an anaerobic digester, the structure has to open up and/or the lignin has to be degraded or removed [13]. Decreased lignin content leads to increased biogas yield. Fernandes et al. [14] and Liew et al. [15] indicated that the biodegradability of rice straw increased with decreasing lignin content, i.e., the higher the lignin content, the lower the biogas production. In order to improve biogas production from rice straw, a pretreatment process is necessary to disrupt the naturally recalcitrant carbohydrate-lignin shields that impair the accessibility of enzymes and microbes to cellulose and hemicellulose [16]. This can be performed by using different pretreatment methods, such as chemically by acids, bases or solvents; mechanically, e.g., by milling; physically by radiation or hydrothermal; and biologically by enzymes or fungi.

The purpose of this paper is to review different pretreatment methods for biogass production from rice straw and to offer an in-depth discussion on the benefits and draw back so feach while striving to present and highlight several combined pretreatment methods.

2. RICE STRAW MATERIAL COMPOSITION

2.1 Cellulose

Cellulose $(C_6H_{10}O_5)_x$, the main constituent of lignocellulosic biomass, is a polysaccharide that consists of a linear chainof D-glucose linked by β-(1,4)-glycosidic bonds to each other. The Cellulose strains are associated together to make cellulose fibrils. Cellulose fibers are linked by a number of intra – and inter molecular

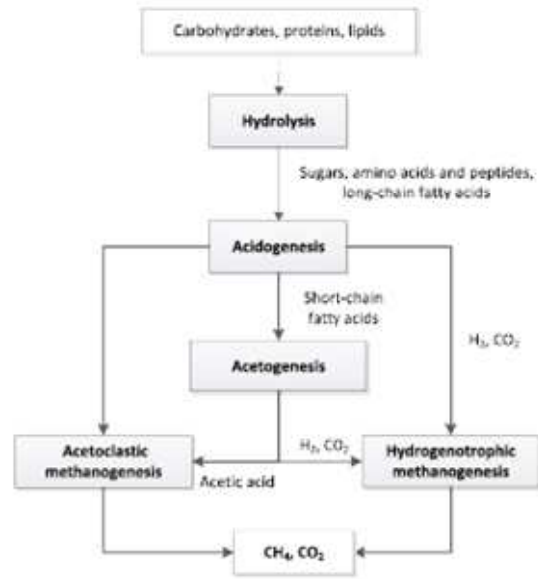hydrogen bonds [18]. Therefore, cellulose is in soluble in water and most organic solvents [19].

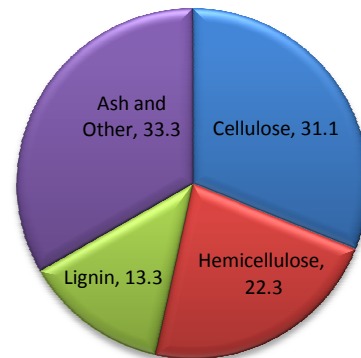Fig. 1. Process flow during anaerobic digestion [17]

Fig 2. Composition of Rice Straw Lignocellulose

2.2 Hemicellulose

Hemicelluloses $(C_5H_8O_4)m$, located in secondary cell walls, are heterogeneous branched biopolymers containing pentoses (β-D-xylose, α-L-arabinose), hexoses (β-D-mannose, β-D-glucose, α-D galactose) and / or urgonic acids (α-D-glucuronic, α-D-4-O-methyl-galacturonic and a-D-galacturonic acids) [20]. They are relatively easy to hydrolyze because of their amorphous, and branched structure (with short lateral chain) as well as their lower molecular weight [18]. In order to increase the digestibility of cellulose, large amounts of hemicelluloses must be removed as they cover cellulose fibrils limiting their availability for the enzymatic hydrolysis [21]. Hemicelluloses are relatively sensitive to operation condition, therefore, parameters such as temperature and retention time must be controlled to avoid the formation of unwanted products such as furfural sand hydroxymthyl furfurals which later inhibit the fermentation process [22].

2.3 Lignin

Lignin $[C9H_{10}O_3(OCH_3)_{0.9-1.7}]_n$ is an aromatic polymer synthesized from phenyl propanoid precursors. The major chemical phenyl propane units of lignin consisting primarily of syringyl, guaiacyl and p-hydroxy phenol are linked together by a set of linkages to make a complicated matrix [23].
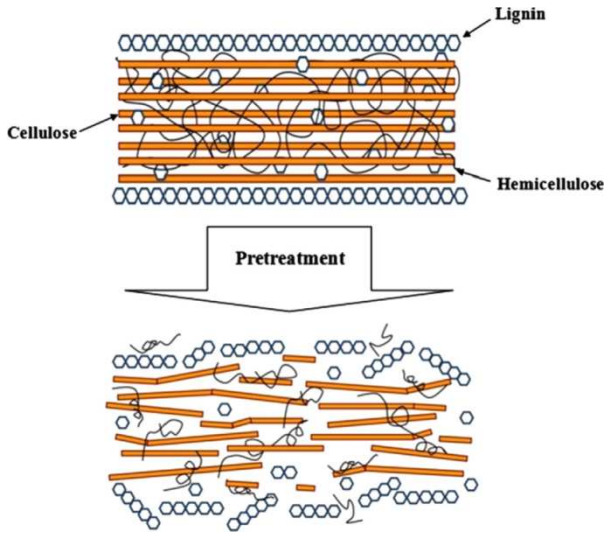

Fig 3. Schematic pretreatment of lignocellulosic material [24]

3.   PRETREATMENT METHODS

PHYSICAL PRETREATMENT
3.1   Hydrothermal pretreatment

Hydrothermal pretreatment use water under high pressure and temperature that can penetrate into the biomass, hydrate cellulose, and removes hemicellulose and part of lignin. The major advantages are no addition of chemicals and no requirement of corrosion resistant materials for hydrolysis reactors in the hydrothermal pretreatment process. The feedstock size reduction is a highly energy demanding operation on a commercial scale. However, there could be no need for size reduction of biomass in hydrothermal pretreatment process and requires much lower need of chemicals for neutralization of the produced hydrolyzate and pr oduces lower amounts of neutralization residues compared to many processes. Hydrothermal pretreatment enhances the accessible and susceptible surface area of the cellulose and makes it more accessible to hydrolytic enzymes [25,26].

Chandra et al. (2012) [6] investigated pretreatments were given to rice straw biomass; hydrothermal (200⁰C, for 10 min) followed by addition of 5% NaOH, in order to maintain appropriate pH suitable for methane fermentation and to avoid the formation of inhibitor during hydrothermal pretreatment. The experimental study revealed that the NaOH and hydrothermal pretreatments to rice straw biomass has improved the biodegradability of rice straw biomass, which is evident from the increased biogas and methane production yields. The result showed biogas and methane production yields as 315.9 L/kg VSa and 132.7 L/kg VSa, respectively, increase of 225.6% in biogas production and 222.0% in methane production relative to untreated rice straw substrate. Hydrothermal pretreatment provided an accelerated pre-hydrolysis of biomass contents during the treatment process and thereby resulted into enhanced biogas and methane production yields.

Hydrothermal pretreated substrate of rice straw has resulted into highest biogas as well as methane production yields. However, it has taken a longer HRT (Hydraulic Retention Time) than the untreated and NaOH pretreated substrates. This is only due to reason that the hydrothermal pretreatment offered an accelerated pre-hydrolysis of the cellulosic and hemicellulosic part of volatile matter during the treatment process. The evidence of this pre-hydrolysis was observed as the pH of rice straw biomass slurry after hydrothermal pretreatment was decreased too low due to production of acids. Therefore, a higher amount of easily degradable volatile matter was available to the methanogenic bacteria for its conversion. Another reason for taking longer HRT is that limited amount/population of bacteria were present in the substrate during degradation process, as the substrate-to-inoculum ratio was 1.0, and the kinetic rate of substrate utilization may have a limiting value to the bacteria. Thus, takes longer HRT to convert available volatile degradable matter into biogas. Furthermore, an increase in HRT may provide sufficient time for methanogens to mineralize the organic volatile matter to methane and carbon dioxide [27]. Therefore, it is very much clear that the hydrothermal pretreatment followed by appropriate amount of NaOH addition is a potentially effective for pretreatment to enhance biogas and methane production yields from the rice straw biomass [6].

3.2   Freeze Pretreatment

Pretreatment is required to alter the structural and chemical composition of feedstock in order to facilitate rapid and efficient hydrolysis of carbohydrates to fermentable sugars. In order to obtain fast enzymatic hydrolysis of feedstock with a high sugar yield, the cell structures need to be broken and porosity must be increased [28]. A novel approach recently developed for physical pretreatment of biomass is the freeze pretreatment and has been found to significantly increase the enzyme digestibility of rice straw. In spite of the high cost involved and that only a few studies have been carried out using this pretreatment so far, its unique features   i.e. lower negative environmental impact, application of less dangerous chemicals and high effectiveness have attracted a great deal of attention [29].

Chang et al., (2011) [29] reported that freeze pretreatment from rice straw improved enzymatic hydrolysis yields by about 84%. Rice straw pretreated by freezing at -20⁰C for 2 hours and the frozen straw was thawed at room temperature for 1 hour. The result showed that freeze pretreatent can reduced sugar yields

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from 226,77 g/kg to 417,27 g/kg and 93,84 g/kg to 138,77 g/kg substrate for 150 U cellulose and 100 U xylanase.

Water volume expands as it freezes, and this is physically related to its crystal structure. Thus, when water cools, it tends to stack in a crystalline lattice configuration that stretches the rotational and vibrational components of the bond. Water, uranium, neon and silicon are some of the few materials that expand when they freeze; most other materials contrary [29]. Pinsky et al. [30] found that freeze-thaw process could disrupt bulk hydration layer, forming a crystal lattice of ice and rendering protein inactive. Other reports [31] have shown that water migrated to form ice crystals during freezing or frozen storage and caused breaking force. Chang et al., (2011) [29] pre-incubated rice straw in acetate buffer for 1 hour. The acetate buffer solute penetrated the pores of the rice straw. As the buffer solute froze, it expanded rapidly, adding accessible surface area and pore volume, while breaking some structures; these processes enhanced the rate of enzymatic hydrolysis.

CHEMICAL PRETREATMENT
3.3 Sodium Carbonate – Sodium Sulfite Pretreatment

Green liquor (mainly composed of sodium carbonate and sodium sulfide) used as a pretreatment of kraft pulping or biomass conversion showed enhanced pulp qualities and promising enzymatic digestibility [32]. Though the existence of sodium sulfide is good for delignification, the elemental sulfur will lead to the complexity of spent liquor handling process as well as environmental contamination if the scale of process is smal [33]. The sulfite can degrade a considerable amount of hemicellulose, reduce the degrees of polymerization of cellulose and xylan, and increase the hydrophilicity of lignin by sulfonation [34]. Na_2CO_3 and Na_2SO_3 pretreatment also have many advantages for commercialization with low technological and environmental risks and barriers [35].

Yang et al. (2013) [35] investigated rice straw pretreated with different ratio of Na_2CO_3 and Na_2SO_3 at 140^0C, chemical charge of 12% for 60 min. At the ratio of 1:0 (i.e., only Na_2CO_3 pretreatment), the increasing Na_2CO_3 charge may intensify the alkaline degradation of polysaccharides, which is mainly peeling reaction. Ester bonds between lignin, hemicellulose and cellulose can be broken, and the lignin macromolecules are degraded [36]. At the ratio of 0:1 (i.e., only Na_2SO_3 pretreatment), except for the more severe alkaline peeling reaction to carbohydrates, the sulfite (SO_3^{2-}) and (or) bisulfite (HSO_3^{1-}) in the pretreatment liquor will lead to the sulfonation of lignin to increase its hydrophilicity, which may promote the subsequent enzymatic hydrolysis process [34]. A higher ratio of Na_2SO_3 in the pretreatment liquor showed better delignification than Na_2CO_3 at the same chemical charge. The delignification capacity of Na_2SO_3 was remarkable even at a relatively low chemical charge, while for that of Na_2CO_3, chemical charge showed

significant impact on its enhanced delignification. Ester bonds between hydroxycinnamic acids and lignin or hemicellulose, cross-linking lignin and hemicellulose are broken during the alkaline degradation [37]. The nucleophilic sulfite (SO_3^{2-}) and (or) bisulfite (HSO_3^{1-}) in the pretreatment liquor (pH 5–9) will lead to the sulfonation of lignin, as well as the cleavage of α- benzyl ether linkages, α-alkyl ether linkages, and β-benzyl ether linkages on phenolic lignin units [38]. The sulfonation can make the lignin more hydrophilic and reduce the hydrophobic interactions with enzymes, which may contribute to the improved enzymatic digestibility of substrate [34].

The highest sugar recovery of pretreated rice straw, 74.5%, 82.7%, and 59.5% for total sugar, glucan, and xylan. The corresponding delignification ratio of pretreated solid was 53.4%, and 91.4% of the polysaccharides were conserved. The sugar recovery of only Na_2CO_3 pretreatment at the ratio of 1:0 was 67.1%, 74.4%, and 53.7% for total sugar, glucan, and xylan. Its corresponding delignification ratio was 40.3%, and polysaccharides conservation ratio was 88.9% [35].

3.4 Hydrogen Peroxide Pretreatment

Hydrogen peroxide (H_2O_2), is a strong oxidant and has been used for biomass pretreatment for both ethanol and biogas production and a well-known reagent in the paper and cellulose industry, is used as a bleaching agent. It has a significant advantage of not leaving residues in the biomass because it degrades into oxygen and water and hardly forms secondary products [39]. H_2O_2 treatment of lignocellulosic biomass partially breaks down lignin and hemicellulose, and releases a cellulose fraction with high degradability to the anaerobic microorganisms. H_2O_2 treatment is a non-selective oxidation process and, therefore, losses of hemicellulose and cellulose can occur.Meanwhile inhibitors might be generated as lignin is oxidized to form soluble aromatic compounds [40]. The H_2O_2 concentration should also be considered because high H_2O_2 concentration (e.g. 4%) was found to inhibit the AD process due to the toxicity of an excess of hydroxyl ions to methanogens [41].

Song et.al (2013) [42] reported that rice straw was pretreated in ambient temperature (25±2)°C for 6,18 day with 2,68% H_2O_2 concentration and 1,08 substrate/inoculum which resulted in a methane yield of 288 mL/g VS. The cellulose and hemicellulose contents in the ground rice straw decreased remarkably in all of the treatments compared with the untreated rice straw. H_2O_2 pretreatment led to considerable cellulose, hemicellulose, and lignin reductions, ranging from 0.9 to 22.0%, 3.7 to 60.3%, and 0.4 to 12.5%, respectively. The most significant reduction in hemicellulose indicates that H_2O_2 is particularly effective in the decomposition of rice straw hemicellulose.

Pretreatment time (PT) has a great effect on the degradation of the main components of agricultural wastes, and that longer treatment times could contribute to increased reductions in the contents of cellulose and

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hemicellulose under certain conditions. At the same pretreatment time (PT), the higher H_2O_2 concentration (HC) resulted in higher decreased cellulose, hemicellulose, and lignin contents. The higher H_2O_2 increased the accessibility of contents to the anaerobic microorganisms, thereby facilitating the usage of soluble compounds with low molecular weights by the microorganisms and thus increasing the biodegradability [42].

3.5 NMMO Pretreatment

Pretreatment with an organic solvent, N-methylmorpholine- N-oxide (NMMO or NMO can dissolve cellulose and efficiently decrease its crystallinity. Moreover, NMMO is an environmentally friendly solvent which can be recovered by more than 98%, with no chemical derivatization and no production of toxic waste pollutants [43]. Compared with other volatile organic cellulose solvents, NMMO possess the advantages of low toxicity, low hydrophobicity, low viscosity, thermal stability, broad selection of anion and cation combinations, enhanced electrochemical stability, high reaction rates, low volatility with potentially minimal environmental impact, and non-flammable properties [44].

Teghammar et al. (2012) [45] reported effect of NMMO pretreatment on digestion of rice straw with 50% w/w NMMO solution after 3 hour pretreatment at 130^0C, while mixing every 15 min, where 328 Nml CH_4/gCH was produced. This production is seven times more than the methane production of the untreated rice straw samples, and corresponds to 79% of the theoretical yield. For the rice straw, 1 or 3 h pretreatments were enough and the longest pretreatment resulted in less biogas. Furthermore, about one week of anaerobic digestion was enough to digest the rice straw samples, even though the experiments went on for six weeks. This means that if the digesting bacteria need no lag phase, just a couple of days should be enough to convert the treated straw to biogas. This improvement is most likely due to the breakdown of the crystalline structure of the lignocelluloses, and consequently a higher accessibility of the bacteria to the cellulose and hemicellulose.

By the chemical action of the solvent, the polar N-O bond in NMMO will break the intra-molecular hydrogen bonds and van der Waals forces stabilizin the cellulose structure, resulting in the formation of new bonds between the solvent and the cellulose. In addition, the NMMO solvent converts the crystallinity of the dissolve cellulose, which further increases the biodegradability [46]. Moreover, the overall mass balances showed no major loss in NMMO pretreatment of hardwood and softwood [47] and no loss in the pretreatment of pure cellulose [46]. This is one of the main advantages of pretreatment of lignocellulose biomass with NMMO compared with similar pretreatment methods. The best digestion of rice straw was obtained after the 1 h pretreatment, and longer pretreatments resulted in lower initial digestion rate and also less methane produced

[45]. Unlike physical and biological pretreatment, chemical pretreatment may leave chemical residues which may influence the downstream AD process. For NMMO pretreatment, it is possible to recover nearly 100% of the used NMMO liquid, so chemical residues might not be a problem [48].

3.6 Alkaline Pretreatment

$Ca(OH)_2$, has been extensively used in improving biodegradability because of its low cost, high recoverability, safe handling, and minor environmental effects [49]. Song et al. 2012) [50] reported that the lignin, cellulose, and hemicellulose of rice straw were significantly degraded, and the highest methane yield of 225,3 ml/g VS, was obtained with 9,81% $Ca(OH)_2$ (w/w TS) for 5,89 day pretreatment time, and 45,12% inoculum content.

Pretreatment time considerably affected the degradation of the main components of rice straw and that long treatments increased the reduction in cellulose and hemicellulose contents under certain conditions. At the same pretreatment time, a high lime concentration resulted in a high decrease in cellulose and hemicelluloses. These results indicate that a high pretreatment concentration more effectively breaks down the lignocellulose matrix and changes its chemical components. The high $Ca(OH)_2$ considerably changed the microstructure of the cell wall and increased the accessibility of contents to anaerobic microorganisms, facilitating the use of soluble compounds with low molecular weights by microorganisms and increasing biodegradability [50]. Lime pretreatment led to limited lignin reduction that ranged from 4.4% to 24.3%, a value considerably lower than those generated by other alkaline chemicals, such as NaOH and $NH_3·H_2O$ [51,52]. Reduced lignin reduction may have resulted from the formation of calcium-lignin complex. Calcium ions, which carry two positive charges, tend to crosslink negatively charged lignin molecules under alkaline conditions is crosslinking is caused by the ionization of functional groups, such as carboxyl, methoxyl, and hydroxyl, through the formation of stoichiometric bonds, thereby weakening lignin solubility by $Ca(OH)_2$ during pretreatment processes [53].

For methane production a certain increase in inoculum amount improved the biodigestibility of rice straw, facilitating its use by anaerobic microorganisms, thereby requiring less time for digestion. Furthermore, the peak value of the pretreatments increased as lime concentration increased but subsequently declined, indicating that a high lime concentration can provide more organic matter to anaerobic microorganisms for biogas generation [50].

Another alkaline used to pretreatment rice straw is NaOH. The results showed that the biogas yield of 6% NaOH-treated rice straw at ambient temperature (20 ± 2 ^0C) for 3 weeks was increased by 27.3-64.5%. The enhancement of the biogas yield was attributed to the improvement of biodegradability of the rice straw

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through NaOH pretreatment. Degradation of 16.4% cellulose, 36.8% hemicellulose, and 28.4% lignin was observed, while water-soluble substances were increased by 122.5%. The ester bond of LCC (lignin-carbohydrate complexes) was destroyed by hydrolysis reactions, resulting in the release of more cellulose for biogas production. The linkages of inter-units and the functional groups of lignin, cellulose, and hemicellulose were either broken down or destroyed, causing intra- and intermolecular changes of chemical structures. The changes of chemical compositions, chemical structure, and physical characteristics made the NaOH-treated rice straw become more available and biodegradable and thus were responsible for the improved biodegradability and enhanced biogas production [54].

However, the utilization of NaOH pretreatment might cause Na^+ ion inhibition of AD processes, especially methanogenesis. Additionally, the disposal of Na^+-containing effluent from AD systems could lead to negative environmental impacts such as soil salinization and water pollution [12]. Chen (2012) [55] has developed an integrated NaOH pretreatment process that includes NaOH recycling to improve biogas yield from rice straw. This process could help to reduce the pretreatment and mitigate the potential environmental pollution caused by waste Na^+ disposal.

3.7 Dilute Acid Pretreatment

Dilute acid is favored over concentrated acid for lignocellulose biomass pretreatment. Dilute acid pretreatment primarily hydrolyzes up to 100% of the hemicellulose into its component sugars (e.g. xylose, arabinose and galactose), depending on the pretreatment conditions [12]. Zhao et al. (2010) [57] reported that dilute acid pretreatment with mixture of acetic-propionic acid was significantly enhanced 35,84% production of methane and about 34,19% lignin was removed and 21,15% the hydrolysis rate was obtained by 0,75% mol/L acid pretreatment for 2 hours at the solid to liquid ratio of 1:20 (w/v).

Acid concentration of 0,75% mol/L can remove rate of hemicellulose and lignin to some extents and thereby enhanced the biodegradability of rice straw as represented by the increase of hydrolysis rate because it could supply more hydrogen ions which can help to solubilize hemicellulose and lignin. Disruption of barriers caused by lignin and hemicellulose made cellulose more accessible to the enzyme and more easily to be converted into fermentable sugars. The longer pretreatment time did not increase the removal of lignin, it was very likely that the structure of lignin was altered and more hemicellulose was removed, thereby enhancing the digestibility of cellulose in the residue solids. The removal amount of lignin depends on the quantity of hydrogen ion in the reaction liquid, that is to say, the lignin removal has a certain value under a fixed acid concentration. It can be concude that dilute acid pretreatment not effective in dissolving lignin but effective for removing hemicellulose [57].

Another study by Hsu et al. 2010) [58] reported a maximal sugar yield of 83% was achieved when the rice straw was pretreated with 1% (w/w) sulfuric acid with a reaction time of 1-5 min at 160^0C or 180^0C, followed by enzymatic hydrolysis. The completely release of sugar (xylose and glucose) increased the pore volume of the pretreated solid residues resulted in an efficiency of 70% for the enzymatic hydrolysis. The extra pore volume was generated by the release of acid-soluble lignin and this resulted in the enzymatic hydrolysis being enhanced by nearly 10%.

BIOLOGICAL PRETREATMENT
3.8 Fungal Pretreatment

Biological pretreatment method is one of alternative methods that not too costly and not cause environmental pollution. Thus, the alternative approach of microbial pretreatment which employs the use of micro-organism especially fungi to increase digestibility of rice straw is the most reliable approach [56].

Sahni and Phutela (2013) [56] reported pretreatment of rice straw with standard culture namely C. versicolor MTCC 138 and isolated lignocellulolytic culture, that is, Fusarium sp. In the case of control (un-inoculated soaked rice straw), there was very little or insignificant change in almost all components, that is, cellulose, hemicellulose, lignin and silica. In the case of rice straw pretreated with C. versicolor MTCC 138 and Fusarium sp. the cellulose content kept on decreasing with the increasing incubation period, with the maximum reduction of 16.8 and 17.2% after 20 days, respectively. Initially, a decreasing trend of hemicellulose content was observed for a period of 15 days in both cultures. But in the case of C. versicolor MTCC 138 pretreated rice straw hemicellulose content increased by 2.7%. Lignin content decreased with the increase of incubation period with maximum reduction of 17.5 and 27.1% in 20 days pretreated rice straw with C. versicolor MTCC 138 and Fusarium sp., respectively. Decrease in silica was smooth and significant with a maximum removal of 25.8 and 16.5% after 20 days pretreated rice straw with C. versicolor MTCC 138 and Fusarium sp., respectively. These observations clearly indicate that C. vesicolor MTCC 138 and Fusarium sp. are ligno-cellulolytic fungus. However, Fusarium sp. could be more potent fungus for delignification as it decreased more in lignin content than C. versicolor MTCC 138.

COMBINED PRETREATMENT
3.9 Chemical + Microwave Irradiation

Microwave irradiation has been widely used in chemistry because it has high heating efficiency and can, in some cases, increase reaction rate and reduce reaction time which could lead to considerable energy savings. However microwave processing might have the side effect of producing heat-induced inhibitors such as phenolic compounds and furfural [58]. As a result, it is important to control pretreatment conditions to avoid the formation of these inhibitors. Therefore, microwave has

not been used individually for lignocellulosic biomass pretreatment, but usually has been used to provide heat for assisting acid or alkaline pretreatment at relatively low temperatures without compromising pretreatment effects [60,61].

Zhu et al. (2005) [62] used microwave and alkali (NaOH) at 700 W for 30 min and 1% NaOH. The result showed that rice straw had a weight loss of 44.6% and composition cellulose 69.2%, lignin 4.9% and hemicellulose 10.2%. The enzymic hydrolysis of pretreated rice straw was also investigated and the results indicate that rice straw pretreated by microwave/alkali had a higher hydrolysis rate and glucose content in the hydrolysate in comparison with the one by alkali alone.

Combination of microwave and chemical pretreatment also reported by Gong et al. (2010) [63] with organic acid (acetic acid and propionic acid). Under optimal conditions (25% acid concentration, 1:15 solid-liquid ratio, 230 W microwave intensity, and 5 min irradiating time), the removal ratios of lignin are 46.1 and 51.54%, and the sugar yields are 71.41 and 80.08%. This suggests that microwave-assisted organic acid pretreatment is effective in improving the enzymatic hydrolysis sugar yield of rice straw. They also reported that the sequence of influence strengths of the factors was microwave intensity > solid-liquid ratio > acetic acid concentration > microwave irradiating time.

Another chemical combined with microwave is hydrogen peroxide (H_2O_2). Under optimum condition (H_2O_2 2%, microwave intensity 100 W, for 3 min) maximum reducing sugar obtained through microwave assisted H_2O_2 is 1,453.64 μg/mL and has a significantly high crystalline index (63.64%) than untreated rice straw sample (52.2%). Microwave assisted H_2O_2 pre-treatmentdisrupted the silicon waxy structure and broken down allether linkages between lignin and carbohydrates and thus, efficiently remove lignin [64].

4. CONCLUSION

Pretreatment rice straw is commonly employed to decrease the recalcitrance of lignocellulosic to anaerobic digestion for increased biogas yield. Pretreatment can decrease crystallinity of cellulose, increase accessible surface area, and reduce lignin content, depending on the functioning mode of the pretreatment methods. Although various pretreatment techniques have been studied, only a few of the reported techniques achieved high biogas yield with low enough costs to be considered attractive. Pretreatment has also been considered as the key cost element in anaerobic digestion of rice straw. Pretreatment processes can also have a significant impact on the configuration, efficiency, and cost of downstream operations. Given the advantages and disadvantages of different pretreatment methods, a successful pretreatment should be able to: (1) improve the digestibility of feedstocks for anaerobic digestion microbes; (2) avoid degradation or loss of carbohydrates; (3) avoid formation of inhibitors; (4) require minimal and inexpensive chemicals or water; (5) avoid costly pretreatment reactors; (6) require limited size reduction; (7) require low energy (heat or power) input; (8) avoid the need for waste disposal; and (9) be cost-effective and environmentally friendly [16,25,64]

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