Overview on Pretreatment Methods of Lignocellulosic Biomass for Efficient production of Biofuels

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Abstract : Biomass available in abundance from the agricultural crop residues such as rice straw, sugarcane bagasse, rice husk etc. are considered to be one of the main renewable energy resources that has great potential to complement the various non-renewable energy resources and can contribute to bioenergy supplies in the world. Although, these residues looks different but all of lignocellulosic nature i.e they are composed of cellulose, hemicellulose and lignin and being of lignocellulosic nature their physiochemical structure and other composition factors provides hindrance in the hydrolysis process to convert the cellulose into the fermentable sugars and other organic compounds and slows down the digestibility through the anaerobic digestion process. So, pretreatment of biomass is the first step for conversion of these residues into biofuels. As pretreatment disrupts the crystalline structure of macro and microfibrils and makes hydrolysis process effective. A number of pretreatment techniques are available at present and are under investigation in laboratory and pilot-plant scales. This paper overviews the various pretreatment methods of Lignocellulosic biomass.

***IndexTerms* – Anaerobic Digestion, Lignocellulosic biomass, Pretreatment, Fermentation .**

I. INTRODUCTION

Agriculture residues, such as rice by-products, sugarcane leftovers, corn straws etc. are available in abundance in most of the developed and developing countries of the world and are considered to be the most promising renewable energy resources which may complement the non-renewable energy resources. As the world population increases, so does the requirement of food and hence, agriculture residues also increases proportionally. Although all of these residues looks different, but are of lignocellulosic nature and composed of cellulose, hemicelluloses, lignin, and other minor compounds. Agricultural wastes lignocellulosic biomass is composition of about 10–25% lignin, 40–50% cellulose and 20–30% hemicellulose,. Cellulose the major structural component of cell wall and hemicelluloses is comprised of repeated polymers of hexoses and pentoses[1]. Lignin provides a protective seal around the other two components i.e. cellulose and hemicelluloses and also protects lignocelluloses against insect attack. The resistance posed by plant cell wall to deconstruction, so as convert the cellulose and hemicelluloses into fermentable sugars and other organic compounds, also known as recalcitrance has to be overcome through combination of chemical and structural changes by different pretreatment methods. So, during hydrolysis process the cell wall has to be opened up, the lignin component of biomass has to be deliginified and separated from hemicelluloses and cellulose.. All these steps are resistant to microbial attack, so pretreatment methods are used to break it apart. In other words, biomass recalcitrance requires pretreatment.

Pretreatment of the lignocellulosic biomass to overcome recalcitrance is the first step required to convert to these biomasses into biofuels. Pretreatment is required to make the cellulose accessible to the enzymes that converts the carbohydrates into fermentable sugars as represented in Fig.1[2-3].

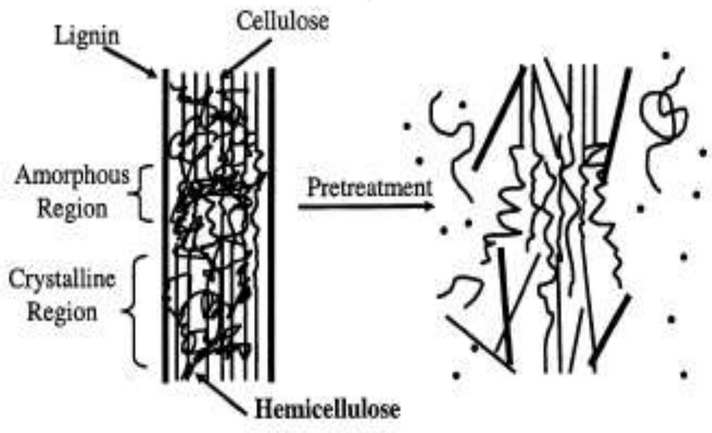

Fig. 1 Effect of Pretreatment [2]

The main objective of the pretreatment is to break the lignin seal and disruption of crystalline structure of cellulose. The selection criteria for opting any of pretreatment the methods includes : (i) the size reduction of biomass should be avoided (ii) hemicelluloses fraction shouldn't be wasted (iii) inhibitors formation should be minimized (iv) energy demand should be minimum (v) pretreatment catalysts should be of low cost and environment friendly. Although, pretreatment is considered to be cost effective technique but it has great potential for improvement of efficiency and lowering the cost through research and development

2. Methods of Pretreatment

Pretreatment of biomass is an essential step to enhance the enzymatic hydrolysis process and can be classified into four main categories physical, chemical, physiochemical and biological. The review of these different pretreatment techniques have been listed below.

2.1 Physical Pretreatment

Milling

Physical pretreatment of biomass involves size reduction through ball milling, grinding, chipping, mechanical extrusion and irradiation. Milling or mechanical grinding can be done through knife, ball milling, hammer, colloid mill etc. The size of biomass can be reduced to 10-30 mm only through chipping however, with the help of ball milling and grinding the size of particles may be reduced to 0.2 mm. Size reduction of particles increases the surface area of biomass to be accessible to the enzymes. However, the specific kind of biomass and duration of milling and types of milling are the main factors which affects the degree of polymerization, increase in the surface area of biomass and disruption in the crystalline structure of Lignocellulosic biomass. Literature shows that disk milling is more effective than hammer milling. It has been observed that the comparison of conventional ball milling and wet disk milling on rice straw results that 89.4% glucose and 54.3% xylose extraction using conventional ball milling and 78.5% glucose and 41.5% xylose using wet disk milling[4-6]. Wet milling disk has advantage that it requires low energy and did not produce inhibitors. Physical size reduction is more effective when it is combined with other pretreatment methods such as chemical pretreatment. Disadvantages for this process include mainly the higher power consumption and its inability to remove lignin.

Mechanical Extrusion

Basically, extrusion is the process in which the objects of fixed material shape can be obtained by forcing it to pass through die of desired cross-section. Mechanical extrusion is the conventional method of biomass pretreatment in which the effect of temperature maintained in barrel combined with shearing force generated by screw blades rotation disrupts the crystalline and amorphous cellulose matrix of biomass. . Karunanithy and Muthukumarappan[7-8] observed that the pretreatments of corn cobs through single screw extruder by varying the screw speeds in the range from 25 to 125 rpm by increasing it 25 rpm per step and extruder temperatures ranging 25 ^{0}C to 125^{0}C alongwith enzymes of different kinds and their ratios observed that 75% of glucose, 49% xylose and 61% of combined sugar recovery at 75 rpm and 125 °C using a cellulase to β-glucosidase in 1:4. In another study, Karunanithy et al.[9-10] observed that the effects of barrel temperatures (50, 75, 100, 150, and 200 °C) and screw speeds (100, 150, and 200 rpm), cellulase with β-glucosidase (1:1 to 1:4) on sugar yield from selected warm season grasses, such as big bluestem, switchgrass,and prairie cord grass. The highest values of sugars yields were obtained as 28.2%, 66.2% and 49.2% from switchgrass, big bluestem, prairie cord grass at screw speeds of 200, 200, and 150 rpm and at barrel temperatures of 75, 150, and 100 °C, respectively, when the ratio of cellulase and β-glucosidase was 1:4. Particle size of biomass plays an important role in overall sugar recovery.

Irradiation

Irradiation includes microwave irradiation, ultrasound, gamma rays and electronic beam to increase the enzymatic hydrolysis of lignocellulosic biomass. Microwave irradiation has several advantages such as low energy requirement, easy operation, high heating capacity in short duration of time and minimum generation of inhibitors. Studies using microwave irradiation technique of physical pretreatment shows that it is more effective with mild alkali reagents.Jackowiak et al. [11-13]worked by using microwave radiation for both switch grass and wheat straw at 150^{0}C. Results showed that pretreatment increases the yield of methane by 28% in comparison with untreated wheat straw. But in case of switch grass no change is observed in the yield of methane . Microwave pretreatment had negative effect on yield of methane and production rate of methane on an energy grass, Pennisetum hybrid at 260^{0}C . Microwave pretreatment was also used for the municipal solid waste but the improvement in biogas production was only 4-7% over untreated material at the temperature range of 115-145^{0}C . In another study on effect of microwave pretreatment on oil palm fruit bunch alongwith alkaline pretreatment results in 74% reduction in lignin[14-15].

Ultrasound pretreatment is relatively new technique used for pretreatment in which waves produces both chemical and physical effects and the morphology of biomass. The duration of sonification and ultrasonic frequency alongwith reactor geometry and type of solvent used influences ultrasound pretreatment on biomass. Prolonged sonification beyond a certain limit has no additional effect in terms of sugar release and delignification. For cellulosic feedstocks, accessibility of cellulose enzymes to cellulose increases with ultrasound irradiation by disrupting the cell wall. Ultrasound pretreatment can enhance sugar yield in the hydrolysis process by changing the surface morphology of lignocellulose materials. Further, it has been observed that combined use of NaOH and Ultrasonic irradiation pretreatment effectively destroys the intermolecular hydrogen bonding of lignocellulose, resulting in one of the more effective pretreatments for enzymatic hydrolysis of bagasse, where more than 90% of the theoretical glucose yield is obtained within 70 h. Combining ultrasonic irradiation and ionic liquids also is an effective pretreatment of lignocellulosic materials, although the effect of this kind of treatment on the physical and chemical properties of lignin still needs further investigation.

Gamma radiations (γ-rays) are very high energy radiations with deep penetration power, consisting of high energy photons, and are produced by the decay of atomic nuclei as they return from high to low energy state. The radioactive nuclides of Cobalt-60 and Cesium-137 produce gamma rays spontaneously when undergoing self-disintegration Radiations then travel from the sealed source at the speed of light and bombard the biomass[16]. The energy carried by the gamma radiation is transferred to the biomass components by collisions of radiations with their atoms. Equal energy is absorbed by the carbon, hydrogen, and oxygen atoms in the biomass polymers. The collisions result in the loss of electrons by atoms causing their ionization. Gamma radiation combined with chemical pretreatment is more effective in enzymatic hydrolysis.

Electron Beam pretreatment uses accelerated beams of electrons to locally irradiate woody material in order to disrupt the structure of cell wall polymers by producing free radicals, inducing cross-linking or chain scission, decrystallization, or decreasing the degree of polymerization. The EB pretreatment method is a cost-effective, efficient, and clean technique. During EB pretreatment, no chemicals are used as solvents or stabilizers, and it thus requires no waste management. EB pretreatment also requires no special temperature, pressure adjustments, or atmospheric, and after pretreatment, no chemical workup is required.

In Pulsed electric field pretreatment the biomass is subjected to sudden high voltage of about 5 to 20 kV per cm for short duration of time at ambient conditions. Application of pulse electric field on waste activated sludge and pig manure in decomposition through anaerobic digestion process shows that methane production enhanced by twofolds from sludge and 80% increase in methane production from pig manure as compared with untreated sludge and manure.

2.2 Chemical Pretreatment

Among all the pretreatment methods, chemical pretreatment seems to most effective in disruption of crystalline structure of biomass. Chemical pretreatment also effective in delignification of biomass and helps to enhance the biogas production through anaerobic digestion. Chemical pretreatment of biomass includes acidic pretreatment, alkaline pretreatment, ionic pretreatment and wet oxidation.

Acidic Pretreatment

Acids such as sulfuric acid, hydrochloric acid, nitric acid etc. are used for the acid pretreatment to increase the enzymatic hydrolysis of biomass. Although acid pretreatment is conventional method used for lignocellulosic biomass pretreatment but it is less attractive due to formation inhibitors byproducts such as ketones, furfurals, phenolic acids etc. Moreover, acidic pretreatment is also of corrosive and toxic nature therefore material required for reactor should be of such quality that it can sustain the required corrosive nature and experimental conditions of acids. Acid pretreatment can be of two types i.e are high temperature for short duration and low temperature for long duration. Sulphuric acid is the most commonly used acid for pretreatment. Pretreatment of rice straw using ammonia followed by sulphuric acid in percolation mode results in better removal of lignin and hemicellulose . In another study, acid pretreatment of wheat and rice straw results in maximum sugar yields of 565 and 287 mg/g respectively with no hydroxymethyl furfural formation. However, disadvantages of producing inhibitory products and corrosion of reactors has led the researchers to look for other acids for pretreatment of lignocellulosic biomass. So, decarboxylic acids such as oxalic acid and maleic acid are tested in order to overcome the disadvantages of sulphuric acid. It has been observed that oxalic acid is less toxic to microorganisms than sulfuric acid. Lee and Jefferies[17] observed in a study on the effect of maleic, oxalic and sulfuric acid pretreatment on the degradation of Lignocellulosic biomass during hydrolysis at the same combined severity factor that xylose and glucose concentrations are maximum in case of maleic acid being followed by oxalic acid and then sulfuric acid.

Alkaline Pretreatment

Alkali pretreatment is considered to be most promising chemical pretreatment method that alters the crystalline structure of biomass and enhances enzymatic hydrolysis without producing inhibitors as in case of acid pretreatment. Alkalis such as sodium hydroxide, calcium hydroxide, potassium hydroxide and ammonia are used for chemical pretreatment of lignocellulosic biomass. A large range from low temperature to high temperature is used for the pretreatment method. But pretreatment conducted at low temperature take relatively long time for the delignification of the biomass [17]. The most popular alkali used to increase the biogas production is sodium hydroxide. It can be used for various lignocellulosic biomasses which involves wheat straw, rice husk, corn stover, sunflower stalks, paper sludge, municipal solid waste etc.

For pretreatment of wheat straw use of 4% NaOH (g/gTS) increased the methane production to 166 L/kg VS from 78 L/kg VS at a temperature of 37^0C for five days [18-19]. Another study on wheat straw also showed 47% increment in biochemical methane potential by using 10% NaOH (g/gTS) for 24 hour . Various loadings of sodium hydroxide (1%, 2.5%, 5% and 7.5%) were used for the pretreatment of corn stover. Results showed that 5% NaOH pretreatment for 24 hour increased the biogas yield by 37% from untreated biomass [20-21]. Zheng et al. [22] used 2% sodium hydroxide for the pretreatment of corn stover for 3 days at 20^0C which increased the biogas production by 72.9% and decrease digestion time by 34.6%.Pretreatment of sugarcane bagasse was done by using 4% CaO (g/gTS) showed that maximum (around 70%) methane production is obtained in first three days and digestion process takes only 8 days. Various feedstocks are treated with CaO and results showed that it had negative effect on the material which are carbohydrate rich. Potassium hydroxide have the effectiveness nearly equal to sodium hydroxide for pretreatment to increase biogas production. Dong et al.[24] used NaOH and KOH both for the pretreatment of the rice husk and result showed that both have the same 50% increment in the biogas yield. But when another study was done by using NaOH and KOH on municipal sludge than KOH produced 13% more biogas in comparison with NaOH [25]. KOH has the similar effectiveness as NaOH, but KOH is much more expensive than NaOH and other alkalis . Hence various studies results shows that

NaOH is most suitable and cost effective alkali used for the pretreatment of lignocellulosic biogas to increase the biogas production.

Ionic Pretreatment

Ionic liquids are salts in liquid form and generally made up of ions and short- lived ion pair. For instance N-methylmorpholine-N-oxide monohydrate (NMMO), 1-allyl-3-methylimidazolium chloride, 1-n-butyl-3 methylimidazolium chloride (BMIMCl), benzyldimethyl (tetradecyl) ammonium chloride etc. NMMO is mainly used ionic liquid for the pretreatment process to increase the yield of biogas produced.Wheat straw was treated with 85% NMMO for 7 hour at 90^0C increased the methane yield by 47%. Along with this, it also increased the porosity of treated straw [26-27]. Another study was also conducted with NMMO on soft woods and results showed that it increases the methane production by 400-1200% and also decreases the time of digestion to only 7 to 10 days . In case of soft wood (agricultural residues) by increasing treatment time the yield of methane also increases except in case of rice straw. One study revealed that when treatment time for rice straw increases from 1-2 hour to 15 hour decreased the methane yield by 3.6 fold [28]. When 85% NMMO was used for empty bunch of oil palm fruit bunch for 3 hour at 120^0C, the enhancement of methane was 48%.

Ionic liquid is a new and effective technique to increase the proper utilization of lignocellulosic biomass. Here the recovery of ionic liquid used for pretreatment is nearly 100%, so leftover chemical is not a problem. But various drawbacks involves its high cost, lack of toxicological data and requirement of regeneration.

wet oxidation

Wet oxidation is a method of pretreatment in which oxidizing agent such as air, hydrogen peroxide and oxygen in addition with water at high temperature and high pressure. Wet oxidation is exothermic reaction and the heat released is satisfactory for maintaining temperature initially at the time of pretreatment. There is high risk of formation of inhibitors such as aromatic compounds and furfural. Mainly this pretreatment is used in the bioethanol production but biogas production is limited [29].

Wet oxidation with hydrogen peroxide on wheat straw and corn stover did not show any positive effect on the biogas yield. Generally this pretreatment is mainly effective on harder wood in comparison with agricultural residue. Addition of sodium carbonate to the wet oxidation pretreatment had a little effect on feedstock of oilseed straw and bean straw but methane production was increased by 34% in case of winter rye feedstock. Additional research is further needed in case of wet oxidation pretreatment.

2.3 Physiochemical Pretreatment

Steam Explosion

Steam explosion method of pretreatment also known as auto hydrolysis is basically a combination of mechanical forces and chemical effects. In this biomass is subjected to high steam pressure at elevated temperature for few seconds to minutes resulting in hydrolysis of hemicelluloses. Then after this pressure is decreased continuously for the termination of the reaction, which leads to an explosive decompression in the biomass. The temperature in this process is typically between 160^0 C to 260^0 C for few seconds to around 20 minutes .Steam explosion treatment was validated on industrial scale at Masonite plants. Steam explosion pretreatment was showed to be an effective method in case of wheat straw as methane yield was increased up to 20-30% in comparison with untreated wheat straw[30-31] .

Steam explosion is used for various kind of lignocellulosic materials for improvement in biogas production . It was also observed that steam explosion increases 40 % methane yield in the secondary digestate of municipal solid waste [32]. Wang et al. reported that pretreatment with steam explosion of bulrush showed 24% higher methane yield than untreated bulrush at steam pressure 1.72 mPa with 8.14 minute of residence time. [33]. while steam explosion has no effect on the biogas production from paper tube residuals, while it shows negative effect when time of pretreatment was increased from 10 to 30 minutes in case of paper tube residuals [34-36].

Thus, Steam explosion pretreatment is one of the most effective technique having various advantages as no recycling cost for waste stream, low pollution level and also low energy cost [37-38]. But special caution must be taken in choosing conditions for the steam explosion pretreatment to avoid the formation of inhibitors and unwanted degradation of the chemical and physical properties of the cellulose.

Liquid hot water

Cooking of lignocellulosic biomass in liquid hot water without using any chemical is also a prominent pretreatment method mainly for pulp industry. Water at high pressure easily breach into the lignocellulosic biomass and it hydrates the cellulose and take out hemicellulose with some part of lignin . Dien et al[39]. used de-starched corn fibre for the liquid hot water pretreatment at 160^0C for 20 minute and it dissolved 75% of the xylan . But when Sreenath et al.[40] used liquid hot water treatment at higher temperature i.e.,220^0 C than it dissolved hemicellulose completely and it partially remove lignin in only 2 minutes .

In another study comparison of liquid hot water and steam pretreatment of sugarcane bagasse was carried out in production of ethanol with temperature range between 170^0C to 230^0C for 1-46 minutes and total solid concentration was 1% to 8% shows that altohugh both pretreatment were effective in hydrolysis but liquid hot water were more effective in xylan recovery than steam treatment [41]. Chandra et al. conducted liquid hot water pretreatment for wheat straw at 200^0C for 10 minute and results showed that methane production from pretreated wheat straw was 20% higher than untreated. And then again using same pretreatment conditions, methane production was checked for rice husk which showed 222% higher methane production than untreated [z, a1]. The main advantage of liquid hot water pretreatment that no chemical is needed, no requirement of corrosion- resistant material for the reactor and lower formation of inhibitors. But liquid hot water mainly removes hemicellulose so mainly two-stage process are used for the pretreatment which is major drawback in some cases.

2.4 Biological Pretreatment

In comparison with chemical and physical methods of pretreatment biological pretreatment considered to be economical, easy and environment friendly pretreatment method. Biological pretreatment involves the use of white rot fungi, brown rot fungi and soft fungi which mainly degrade lignin and hemicelluloses with lesser amount of cellulose. However, the degradation process of biomass through biological pretreatment is very slow process therefore not favorable method among industries. Several studies on biological pretreatment along chemical and physical pretreatment is more effective than biological pretreatment alone. *Potumarthi* te. Al. obsereved in a study on pretreatment of rice husks by fungus Phanerochaete chrysosporium that 44.7 % sugars reduction was there. Further, more studies shows that performing fermentation and saccharification processes at high-substrate concentration results in increase in the concentration of inhibitors. Pretreatment with enzymes has been suggested to prevent production of such inhibitors . In another study Martins et al. [42-44] showed that 33 % more recovery of phenolic compounds in the leaves of Larrea tridentata was found in combination of biological pretreatment followed by methanol extraction compared to methanol extraction alone.

Conclusion

The various studies on the pretreatment of Lignocellulosic biomass was discussed here with there specific advantages and disadvantages. Each biomass consists of a significant quantity of lignin which inhibits the process of hydrolysis of hemicelluloses and cellulose. This has led the researchers to do extensive research in pretreatment techniques of biomasses. Although combination of various pretreatment methods are seems to be more effective in the hydrolysis process but not a single method in itself has potential for complete delignification of biomasses in an economic and eco-friendly way. Hence, a extensive research in this field of pretreatment is still required involving either invention of new methods or upgradation of existing methods of pretreatment. Therefore the need of hour is to develop the models that may help for the selection, optimization techniques, design, and process control pretreatment technologies that can match the biomass feedstock with the appropriate method of pretreatment depending on their compositional characteristics and applications.

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