A Critical Review on the Various Pretreatment Technologies of Lignocellulosic Materials

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Abstract

Nowadays, finding new sources of renewable energy is an absolutely essential need for human. Production of biofuel is a suitable way to find such a renewable energy source. Pretreatment is considered as an important step for biofuel production. The aim of this study was to collect recent achievements in pretreatment techniques to have a comprehensive and precious source about this topic. In this study many pretreatment techniques: microwaves, biological, alkaline, ionic liquid, organic solvent, acidic, mechanical, pyrolysis, steam, wet oxidation, ammonia fiber explosion and liquid hot techniques have been introduced. Although several new techniques have been developed to pretreatment of lignocellulosic biomasses, many obstacles are still needed to be overcome to use these techniques for industrial application.

Keywords: Lignocellulosic biomass, Pretreatment, Biofuel production, Energy production

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1 Introduction

Energy demand is increased every day by developing industries (1). Nowadays, fossil fuels are considered as main source of energy worldwide (2). Since fossil fuels are not renewable, many studies have been carried out to find alternative energy sources (3). Therefore, lignocellulosic biomass conversion to biological fuels has attracted a huge amount of scientist’s attention (4). Pretreatment process is the first stage for biomass conversion to biofuel. Many studies reported the importance of pretreatment step on biofuel production processes (5). The well-known technique for biomass pretreatment is thermochemical technique. This techniques is faced whit several economic, environmental, and technical difficulties. That is why finding more appropriate pretreatment techniques for biofuels production such as biohydrogen, biogas, and bioalcohols is necessary. Lignocellulosic biomasses are inexpensive and abundance; therefore, these types of biomasses are attractive to be used as row materials for biofuel production (6). Raw lignocellulosic biomass cannot easily used for biofuel production due to existence of some recalcitrant compounds and very complex structure (7). Consequently, pretreatment is so important to have a fast and efficient conversion of lignocellulosic biomasses to final products. Several futures have been introduced for an ideal pretreatment technique such as feasible and effective with high solids loadings, lower energy demand and moderate cost, preserving solubilized carbohydrates, avoiding formation of inhibitors to the subsequent fermentation step,
producing highly digestible feedstock, and little or no biomass size reduction (8). Although many pretreatment techniques have been developed by scientists, there is no technique that to have all the above mentioned futures. Various developed techniques for pretreatment of lignocellulosic biomass have been categorized in Figure 1. There also some reports about generation of inhibitory substances within the process of pretreatment (9). Pretreating several particular biomasses causes production of toxic compounds (9). The most important toxic compounds generated during pretreatment processes of lignin are aromatic compounds, ketones, aldehydes, organic acids, and furans (10). Pretreatment is an influential technique on other steps of biofuel production. Pentose and hexoses can be converted to inhibitory substances such as furfural and hydroxymethylfurfural within pretreatment processes. The amount of produced sugar and biofuel and be significantly decreased when toxic compounds are presented in the environment.

2 Effecting parameters

2.1 Delignification

Elimination of lignin from lignocellulosic biomasses (such as woody tissue) using different natural enzymatic or chemical methods is known as delignification. Nowadays, many methods have been introduced to produce energy in various forms such as pyrolytic biooil, biodiesel, and biogas (5, 11-14). Bioethanol production is the most important way to produce energy from ligninocellulosic biomass compared to other energy sources such as biogas, pyrolytic oil, and biodiesel (10). Abundance and low cost of lignocellulosic biomass is the main reason for selection of this type of biomass to produce different energy sources like bioethanol. Lignocellulosic biomass has low amount of oil and that’s why this type of biomass is not suitable for production of biodiesel. Biogas are usually utilized for generation of thermal or electricity energy and it is not used as a vehicle fuel. Biodiesel is another important technology of energy conversion. Trans-esterification process of animal fats and vegetable oils is a way to generate biodiesel. Biodiesel is mostly achieved from specific type of plants such as rubber seed (15), coconut (10), mahuva (16), tobacco seed (17), castor (18), Eruca sativa (19), pongamia (20), and jojoba (21, 22). Also usage of some other plants like palm oil, sunflower, flax, pongamia, jatropha, and mustard have been reported to produce biodiesel (10). Lignocellulosic biomass do not has oils that are necessary for biodiesel generation. Although some crops such as mustard has oils they are used for animal feed. Fresh oil of vegetable has a viscosity between 28 and 40 mm²/s. Direct usage of vegetable oil as diesel engine fuel is not suitable and can make problems for the diesel engines including deposits formation and injector coking arising from poor atomization due to its high viscosity (23). A study showed that the present economics of ethanol produced based on molasses could not be appropriate for commercial blending of ethanol in petrol. This study also demonstrated that nearly 736.5 million ton of sugarcane is require if Indian government aim to have 10% blending of biodiesel and diesel fuel. It means that Indian government need to have 10.5 million hectare for sugarcane cultivation (24). Sugarcane require a large amount of water to grow (20000–30000 m³/ha); therefore, cultivation of this plant is faced with several difficulties (24). Based on the above mentioned explanations, it is necessary to find an alternative way to produce biofuels. Lignocellulosic biomasses including cereal straws which are widely cultivated worldwide may consider as a suitable feedstock for biofuel production. Cereal straws are usually burned by farmers which produces a large amount of air pollutants (25). Several inexpensive lignocellulosics agricultural waste are accessible such as wheat straw, rice straw, softwood, switch grass, salix, willow, timber species, rice hull, and sugarcane bagasse as a feedstock for biofuel production. In some countries that have a wide agricultural activities the agricultural wastes have a good potential to produce biofuels. Different biofuel production yields can be obtained using various crops. The cost of biofuel production depends on the cost of agricultural wastes, transportation method of agricultural wastes from farms to factories, and processing technology. Also, government policies about biofuel production can be considered as an influential factor on biofuel cost. The cost of biofuel production and market price are other factors which are effective on final biofuel cost. Seasonal availability of agricultural wastes depend on the type of it; for example cotton stalk is available between January and March whereas maize stalk is available from August and December. Information about seasonal availability of agricultural wastes is very important to guarantee the feedstock availability all over the year for the biofuel factory. The most important part of plant cell wall is composed of lignocellulos. Lignocelluloses is a natural and complex composite including lignin, hemicellulose, and biopolymers—cellulose (26, 27). Some other materials such as ash can be found herewith lignocellulosic biomass. Lignocellulosic biomass is a heterogeneous composite of lignin and carbohydrate polymers which contains up to 75% of carbohydrates (based on dry weight) (24). Lignocellulosic biomass contains complex sugars; therefore, it is not readily converted to biofuel. Also, it is contains several polysaccharides including hemi-cellulouse and cellulose which require to be converted to the monosaccharide. Lignin, hemicellulose, and Cellulose are strictly associated with each other so this association can almost stop the access to the hydrolytic agents. The lignin should be eliminated or modified to access the hydrolytic agents using different chemical or biological techniques (28). Cellulose which is also known as cellulobios is considered as a polymer of glucose. The cellulose structure aid to have a tightly packed polymer chains, resistant to depolymerization, and highly crystalline structure (29). Another carbohydrate component which is found in the lignocellulosic biomass is hemicellulose. This compound is composed of 5 and 6 carbon sugars that has an amorphous, branched, and random structure. Both the hemicellulose and cellulose are polymers of sugars; therefore, they are considered as a potential source of fermentable sugars. Both the hemicellulose and cellulose can be simply processed into other various products (30-33). Although, many difficulties have been introduced for biofuel production, existence of lignin is the most important one. Lignin is a very stable biopolymer built from three cross-linked phenylpropane units of p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (34) which are bonded together with over two-thirds being ether bonds (C–O–C) and the rest C–C bonds (34).
Lignin is hydrolyzed using cleavage of the ether bonds that are catalyzed by water molecules and hydrogen or hydroxyl ions (36). Ash content of lignocellulosic biomasses is usually composed of minerals such as sodium, magnesium, calcium, aluminum, and silicon. Extractives are other negligible compounds found in the lignocellulosic biomass that include minerals, salts, phytosterols, phenolics, fatty acids, resins, and fats. Delignification using biological techniques has three main steps: (a) first step is lignocellulose pretreatment that can convert lignocelluloses as recalcitrant structure to reactive cellulosic intermediates; (b) enzymatic hydrolysis in which cellulose hydrolyze using reactive intermediates to fermentable sugars such as xylose and glucose; and (c) fermentation process that can produce biofuel or some bio-based compounds like succinic acid or lactic acid (37-40). The delignification of ligninocellulosic biomass is illustrated in Figure 2. Ligninocellulosic biomass can be biologically or chemically degradable after removal of recalcitrant compounds from the biomass (41). There are several explanations for the importance of delignification
which are introduced by many researchers (9, 42). An ideal delignification must have following futures: very limited production of sugar; very limited amount of residual lignin; producing a very high degradable cellulose, very low amount of required energy, low required cost; and ability to recover nearly all carbohydrate. The delignification process is the most important and difficult steps in biofuel production. It was reported that delignification has an intensive effect on all next steps in the biofuel production (9). Although lignin should be eliminated using pretreatment techniques for enhancement of biofuel production, recent studies show that lignin may be used in construction industry, dust particle controls, cleaning metallic surfaces, chemical coatings, agro farmland improvements, and paint industry (10).

2.2 Enzymatic hydrolysis
Using an optimized enzymatic treatment process such as utilization of accessory enzyme including laccase and xylanases may decrease the concentrations of the enzymes required. It can also improve the cost-effectiveness of biofuels generation. The lignocellulosics materials digestibility using enzymes depends on the level of crystallization, lignification, and acetylation processes (43). An extensive delignification is needed for achieving a suitable digestibility regardless of crystallinity and acetyl content. Delignification and deacetylation cause enzymatic hydrolysis and crystallinity not to stop. This does affect initial hydrolysis rates but does not significantly affect sugar yields (43). Studies showed that the size of ligninocellulosic biomass (except large chunks) has not an significant influence on enzymatic digestibility of bagasse (10), switch grass (43), corn stover (44). It has been reported that the effectiveness of the absorbed enzymes and enzyme adsorption are influential factors on enzymatic hydrolysis rate (45). The effectiveness of the enzyme can be enhanced after lignin removal since non-reproductive adsorption site is eliminated using raising access to cellulose and hemicellulose (holocellulose). The covalent linkages and physical binding between lignin and hemicellulosic grass cell walls affects enzymatic hydrolysis (46). Therefore, enzymatic hydrolysis of wheat straw for biofuel generation is bottle-necked by the limitation of their efficacy and the cost of enzymes (13).

3 Types of pretreatments
A costly step in lignocellulosic biomass conversion is pretreatment. This step can be done by chemical, physical or hybrid techniques which are generally energy intensive. The most important techniques for pretreatment are presented in the next sections.

3.1 Microwave assisted technique
Using microwaves is another way for pretreating of lignocellulosic biomass. Microwaves is an electromagnetic wave with wavelength between radio waves and infrared radiation. Microwave radiation for pretreatment of lignocellulos in comparison with hydrothermal technique has many advantages such as lower the reaction activation energy, enable more rapid product formation, and reduce the reaction time remarkably (47). Such advantages make microwave technique as a promising technique for pretreatment of lignocellulosic biomass. The conventional pretreatment techniques such as autohydrolysis, steam explosion, and dilut acid pretreatment must be done at high pressure and temperature. These pretreatment techniques are able to break complex chemical bonds of lignin-carbohydrate, lignin, and hemicellulose. In this condition cellulose can be exposed to cellulase attacking. Usually, lignocellulosic biomass should be heated between 160 and 250°C. The heat can be provided using indirect heat conduction or injection of high pressure steam. When the conventional pretreatment techniques are utilized, the row lignocellulosic biomass should be crushed to small pieces due to saving energy. Hemicellulose is converted to furfural and even to humic acids during the pretreatment process which is adverse to fermentable sugars recovery and conversion. Microwave technique is able to heat lignocellulosic biomasses quickly and uniformly. When microwave technique is applied for pretreatment of lignocellulosic biomass, the above mentioned difficulties can be avoided. Pretreatment using microwave was firstly introduced by Ooshima et al. (1984). After that a remarkable progress on using microwave pretreatment techniques such as designing particular microwave vessels for loading biomass and new microwave reactors has been observed (7). Usage of high boiling solvent and microwave technique was also used by (48). They showed that the yield of levoglucosan from fast pyrolysis of corncobs could 189 times increase when corncobs were pretreated by microwave at 150 W for 18 min and glycerol as high boiling solvent. Additionally, the results demonstrated that the alkali and alkaline earth metals and ash could be effectively removed from corncobs using microwave and glycerol (48).

Figure 2: Fractionation of lignocellulosic biomass (35)
Salt ions have more movement in electric field compared with pure water; therefore, the heat of salt solution can increase faster to the expecting temperature. Studies on the pretreatment using salt solution and microwave radiation demonstrated that solution containing salts can be heated sooner than that without salt ions (49). (50) applied calcium chloride under microwave radiation for pretreatment of corn stover. They could find that residence time and temperature were the most effective parameters on the corn stover enzymatic digestibility. The optimal temperature and residence time with solid-to-liquid ratio (w/v) at 10% were 162°C and 12 min, respectively. They reported that under optimum condition enzymatic hydrolysis ratio was 90.66%. Although higher amount of calcium chloride can decrease the required temperature for pretreatment of corn stover, it was difficult to separate it from solution after finishing the process (50). Pretreatment of lignocellulosic biomasses can be efficiently pretreated by acid (51). Microwave can be used as a suitable alternative for increasing temperature in acid pretreatment technique. Using microwave radiation not only could decrease the resident time but also could increase the performance of pretreatment.

Unlike lignocellulosic biomass pretreatment at atmospheric pressure microwave, high pressure microwave should be done in closed reactors. The range of temperature in this type of reactors is between 150 and 250°C. In high pressure microwave technique, higher temperatures can reduce the resident time and increase performance for pretreatment. Using the microwave pretreatment under high-pressure require a more complex reactor since microwaves propagate in a “closed” reactor. This dynamic pretreatment reactor could use theoretically for continuous pretreating of lignocellulosic biomasses. Since lignocellulosic biomasses are insoluble in water, they cannot be easily pumped into the pipes. Lignocellulosic biomasses should be crushed to small particles and then suspended into a large volume of a liquid such as water. Next it can be transferred using pipes. It was reported that a ratio of liquid–solid as much as 50:1 is suitable for transferring lignocellulosic biomasses using pipes. Application of such a big liquid–solid ration can increase the consumption of energy by a microwave reactor which it reduce the economic viability of pretreatment (52). A continuous microwave reactor was designed for biomass pretreatment in a pilot scale and its power of microwave was linearly varied from 0 and 6 kW (53). Their highest capacity of pretreatment using this microwave reactor was 5 kg/h. They used a transport belt to transfer the biomass toward the microwave reactor which was a good idea for solid materials including corn stover. The ratio of liquid to slid and also the require energy to transfer corn stover was reduced using the transport belt. This microwave reactor needed high boiling organic solvent since it should be run at atmospheric pressure. Using high boiling organic solvent increased the cost of this type of reactor. The effect of using various heating sources for pretreatment of switchgrass was investigated by (54). At the same temperature (190°C) and resident time (30 min) pretreatment of switchgrass using microwave could achieved an enzymatic hydrolysis ratio of 58.5% that was 53% greater than that by conventional heating source. An acerbic organic solvent was applied as absorbing medium of the microwave to pretreat softwood by two groups of scientists (55, 56). They demonstrated that ratio of hydrolysis of polysaccharides to soluble sugars was enhanced by 5.23% compared to that with conventional heating. Ferric sulfate was used for pretreatment of bamboo using microwave as source of heating (57). The results illustrated that the ratio of cellulose enzymatic hydrolysis was raised from 52.72% to 72.15% by pretreatment using microwave.

3.2 Alkaline technique

The removal of some recalcitrant compounds including various uronic, acetyl groups, lignin, and acid substitution from lignocellulosic biomasses is an essential duty of a pretreatment technique. The cellulose and hemicelluloses solubilization in alkaline pretreatment technique is not effective as much as other pretreatment techniques such as hydrothermal or acid. In the other hand this technique needs lower operation temperature but it require a longer residence time (between hours and days). Generally, sodium hydroxide have been employed as a basic catalysts (58). In an alkaline pretreatment, sodium hydroxide solution was applied to improve generation of biogas from residues of herbal-extraction process (59). They demonstrated that 72.1% of raw materials weight was reduced during the biogas generation. Sodium hydroxide solution was used for pretreatment of microcrystalline cellulose (60). They reported that the performance of pretreatment can be increased at higher alkalinity and temperature. Their results showed that the samples could be completely converted to glucose. The theoretical investigations revealed that the maximum yield of ethanol was around 59% for the samples pretreated by sodium hydroxide. The method of Box and Behnken Design was applied to study the influence of substrate concentration, resident time, and alkali concentration and on the hydrolysis of polysaccharides to soluble sugars of rice straw and hulls (61). The outcome demonstrated that the best pretreatment conditions were substrate concentration 30 g/L, heating time of 22.50 min, and alkali concentration 2.75% (61). Orthogonal design was used by (62) to find the optimum condition of wheat straw for bioethanol production. The highest yield of bioethanol production was achieved with heating time of 15 min, 10 Kg sodium hydroxide/m³, and 80 g biomass/kg.

3.3 Ionic liquid technique

Nowadays, using ionic liquids with microwave radiation for pretreatment of lignocellulosic biomass has been attracted attention of a large number if scientists. Ionic liquids showed a very high solubility of biomass which made it perfect for lignocellulosic biomass pretreatment. Dissolution of cellulose using ionic liquids was investigated by (63). This ionic liquid was composed of many cations and anions such as 1-butyl-3-methylimidazolium, chloride ion, bromine and thiocyanate (63) reported that nearly 25% of cellulose was able to dissolve in 1-butyl-3-methylimidazolium when it was heated. A ionic liquid containing 1-ethyl-3-methylimidazolium-acetate, 1-ethyl-3-methyl imidazolium diethyl, 1-butyl-3-methylimidazolium chloride, and 1-allyl-3-methylly midazolium-chloride have been intensively investigated due to their notable cellulose dissolution ability (64). The pretreatment of lignocellulosic biomass using ionic liquids is an expensive technique. Also, it needs a large amount of energy to recycle pure ionic liquids. Furthermore,
viscosity of ionic liquids is gradually increased that makes it challenging to handle.

3.4 Organic solvent technique
Since lignocellulosic biomasses have a high boiling point at atmospheric pressure, many high boiling organic solvents such as glycerine and 1,4-butanol are usually applied for biomass pretreatment. Usage of high boiling organic solvents at high temperature can break the bonds between biomass and lignin and they finally are dissolved into the organic solvent to be recovered as a by-product. The residual materials can be easily degraded after removal of lignin. During this process organic solvent can be recycled which is considered as an advantage of organic solvent technique. Moretti et al. (2014) used different organic solvents (phosphoric acid, glycerol, and water) for pretreatment of bagasse. They could found that this technique is more effective to hydrolyze sugarcane bagasse when glycerol was used as solvent (65). They also found that when glycerol was used as their solvent for pretreatment, the yield of sugars reduction was 12 times higher than water and phosphoric acid. The experiments showed that 5.4% and 11.3% of xylan and lignin, respectively were degraded during pretreatment of sugarcane bagasse using glycerol which might be the reason of high reducing sugars in this technique (65). It was reported that simultaneous usage of glycercine can be used for pretreatment of rice straw (7). The reduction of sugars in this way was 2 times higher than the control. It was reported that temperature was an effective parameters on pretreatment performance at more than 160°C while it is not effective under lower than 120°C. Plant cellulose, alkaline glycerol, aqueous glycerol, and water as solvent for pretreatment of rice husk and corn straw. They reported that using glycerol as the high boiling solvent could partially remove lignin from rice husk while alkaline glycerol was not able to remove lignin. They also reported that using either glycerol or alkaline glycerol as organic solvent is effective for removal of lignin from corn straw (66). Excitingly, the maximum yields of hydrolysis of polysaccharides to soluble sugars were achieved for both rice husk and corn straw pretreated using alkaline glycerol. Analysis of corn straw structure showed that pretreatment cause a dramatic change on its structure. These results illustrated that the type of organic solvent should be selected based on application of biomass (66).

3.5 Acid technique
The degradation speed of lignocellulose pretreatment such as liquid hot water, hydrothermal and un-catalyzed steam explosion can be increased using catalysts (67, 68). Different bases and acids have been applied for lignocellulose pretreatment (69). Some acids including phosphoric acid, acetic acid, and sulfuric acid have been commonly utilized as catalysts (8). Additionally, lignocellulose biomasses at high-temperature processing were able to release various acids such as acetic acid that might be used as the catalyst for autohydrolysis (70).

Pretreatment of lignocellulosic biomasses at acidic condition could convert hemicelluloses into soluble sugar; therefore, the cellulose could be simply degraded due to changing in the structure of biomass. Increasing of temperature can enhance the speed of hemicelluloses conversion in dilute acid pretreatment. Several methods such as burning natural gases or microwave techniques can be used for increasing the temperature. The highest yield of surge reduction was achieved as much as 48.3 g for each 100 g pretreated hyacinth in an environment containing 1% sulfuric acid environment. In this condition 96% of surge was converted (51). Starch-free wheat fibers was pretreated in a low concentration of sulfuric acid (71). They found that using microwave as heating source is more effective than steam for the acid pretreatment. The effects of temperature on the structure of lignocellulosic biomasses with a 0.2 M sulfuric acid was studied (72). They showed that the increasing of temperature had positive effects on the destruction of biomass structure during acid pretreatment. The pH of water somewhat depends on temperature; for example: pure water has a pH of 6.99 at 25°C. The pH of pure water at 150, 200 and 250°C would be decreased to .5.52, 5.16 and 4.88 (73). This phenomenon is due to presence of weak acids in the water. Therefore, conventional hydrothermal pretreatment techniques or microwave pretreatment can be partially categorized as acid pretreatment techniques (7).

The degradation of hemicellulose can be increased when acid is used for pretreatment of lignocellulosic biomasses. It is reported that up to 100% of hemicellulose can be eliminated when acid technique is used (74). Plant cell wall contains two important compounds: hemicellulose and lignin. These compounds have been linked by three main co-valent bonds for formation of lignin–carbohydrate complexes (75). Lignin–carbohydrate complexes are considered as recalcitrant compounds in lignocellulosic biomass. The degradation of hemicellulose causes rearrangement of lignin molecular structure. In this case, cellulose is exposed by cellulase enzyme; therefore, the rate and proportion of cellulose degradation will be enhanced (76). Present of sulfur oxide shows some particular advantages as hydroysis catalyst over sulfuric acid. Sulfur dioxide can be added either with the steam or ahead of reactor. It is better distribute sulfur dioxide through the biomass to have a uniform reaction and decrease the cost. It was reported that hemicellulose and cellulose hydrolysis in many types of lignocellulosic biomasses such as corn cobs, wheat straw, sugarcane bagasse, aspen poplar chips and pine sawmill residues in present of sulfur dioxide can be done at temperatures 150 °C and 190 °C, respectively.

3.7 Biological techniques
Biological pretreatment techniques are considered as one of the important techniques because it uses natural microorganisms or their enzymes (77-79). Biological techniques have many advantages such as no obligation to recycle the chemical compounds after pretreatment, low downstream processing costs, no or minimum inhibitor formation, simple operating conditions and equipment and low energy consumption (80, 81). Therefore, biological pretreatment is an inexpensive, safe, and environmental friendly technique for pretreatment of biomass. Value added products may be produced during biological pretreatment of lignocellulosic biomasses which make it an economic technique. Biological pretreatment of lignocellulosic biomasses is able to convert lignin into different simpler compounds which can be utilized as the starting materials for production of syringaldehyde, benzoic acid, cinnamic acid, vanillic acid, vanillin, and phenolic acids (82). Also, biological pretreatment of microalgae can produce carbohydrates,
proteins, and lipid derived compounds. These compounds can be applied to produce livestock feed, fine chemicals for pharmaceuticals, and food supplements (83). The combination of biological pretreatment and bio-refinery can enhance the sustainability during generation of biofuels. This combination showed an environmental friendly and cost-effective way to produce biofuel (84). Although the technique of biological pretreatment has potential of implementation on large scale, it has not yet been used for commercial purposes due to some reasons such as low downstream yields, loss of carbohydrates, and long pretreatment time (85). Several studies have been carried out on biological pretreatment of lignocellulosic biomass and microalgae which shows a promising results compared to the results achieved from using biomass without pretreatment (86, 87). Although the number of studies on biological pretreatment of lignocelluluses is very higher than microalgae, utilization of this technique is more effective for microalgae. Zabed et al. reported that microalgal composition and structure are more appropriate for biological pretreatment; therefore, this technique is more effective for microalgae (88). Lignocelluluses have high quantity of lignin in their cell walls while microalgae have protein, lipid, and starch, without any lignin (89). Sometimes lignocelluluses is pretreated for removal of lignin to enhance cellulose digestibility (90). In addition, rupturing the cell walls and the macromolecules hydrolysis can be the main reason for pretreatment of microalgae (91, 92). The reasons for pretreatment of lignocellulosic biomasses can be changed depending on the types of biofuels and the biological pretreatment method that is applied. For instance, biogas generation using anaerobic reactor goals to hydrolyze the macromolecules without expecting a separate delignification process for lignocellulosic biomass (93, 94). There is no enough technical information for using biological pretreatment of lignocellulosic biomass in large scale; therefore, more studies should be done to collect these technical information.

3.8 Mechanical techniques

Several kind of techniques are introduced to reduce the size of lignocellulosic biomass including milling, grinding, shredding, and chipping for increasing its digestibility (95). Mechanical pretreatment technique can enhance the specific surface area and reduce the degree of cellulose crystallinity and polymerization (96). The size of materials in various mechanical techniques is different. Chipping can produce materials with size of between 10 and 30 mm, grinding and milling have a better performance and they can produce materials with size of between 10 and 30 mm. Two factors are important in mechanical comminution: first, biomass characteristics; second final particle size. These can determine how much energy would be needed for the above mentioned comminution. The needed energy for lignocellulosic biomasses such as hardwoods is higher than agricultural wastes (97). Although some reports shows that the biofuel production can be enhanced when the lignocellulosic biomass was milled (98), it is not cost-effective due to its high energy consumption on large scale. Many researches have also investigated that milling after chemical pretreatment can decrease (e) the generation of fermentation inhibitors, (d) liquid to solid ratio, (c) energy needed for mixing of pretreatment slurries, (b) cost of separation of solid liquid because the pretreated lignocellulosic biomass is simply separated, and (a) required energy for milling (99, 100). There are many kinds of milling processes including hammer milling, disk milling, ball milling, and vibratory milling used to increase enzymatic hydrolysis (101). The reports shows that vibratory ball milling is a more effective technique compared to ball milling technique to decrease cellulose crystallinity of aspen and spruce chips (10). Also, disk milling that is able to produce fibers is more effectively increases hydrolysis of cellulose compared to hammer milling which produces finer bundles (100).

3.9 Pyrolysis

Lignocellulosic biomass can be pretreated using pyrolysis technique. Cellulose can be decomposed into residual char and several gaseous products at temperature more than 300°C. it should be noted that the rate of cellulose decomposition at temperatures less than 300°C is very low. It was reported that hydrolysis of lignocellulosic biomass pretreated by pyrolysis technique using a 1 N sulfuric acid can convert 80–85% of cellulose into reducing sugars with more than 50% glucose (102).

3.10 Steam pretreatment

In steam pretreatment technique, Lignocellulosic biomass can be pretreated with high pressure saturated steam (0.7 to 4.8 MPa) at temperatures from 160 to 240°C. Several reports showed that pretreatment using steam is able to hydrolyze the hemicelluloses and modify the lignin. It can also enhance the surface area and reduce the degree of polymerization and the cellulose crystallinity (103). Corn stover pretreatment using steam with and without sulfur dioxide was studied by (74). There are some reports to show that existence few amount of xylanases can have a great effect on xylose production. These reports demonstrated that the glucose yield rose from 69% to 94% (9, 74). Similar results have been also reported by other scientists (9, 104, 105). Approximately, the overall yield of glucose and xylose during pretreating corn stover with steam at 190 °C for 5 min along with sulfur dioxide were 90% of and 80%, respectively (106). The extended delignification, with increasing temperature, strongly affects the strength properties (107). It is possible to produce ethanol from lignocellulosic biomass by steam pretreatment, enzymatic hydrolysis and fermentation. An important factor to have a cost-effective production of ethanol is the sugar yields, from both cellulose and hemicellulose (74). One of the advantages of using steam pretreatment is that it can rapidly increase the temperature without excessive dilution of the resulting sugars (8). The rapid increases of pressure aids in defibrillating the cellulose bundles which improves the cellulose availability for fermentation and enzymatic hydrolysis (108). Stem pretreatment has two main steps: auto-hydrolysis and depressurization. Within auto-hydrolysis step, high temperature is used which can improve the acetic acid formation from acetyl groups connected with hemicellulose. This step leads to hemicellulose hydrolysis. The acetic acid formed further catalyzes the hydrolysis of the hemicelluloses. In depressurization step the size of biomass particle are reduce which increase the cellulose enzymatic accessibility. It was reported that steam pretreatment is an efficient technique for corn stover biomass (109). Steam pretreatment is able to efficiently breakdown the lignocellulosic structure, defibrillation, depolymerization of the lignin components,
and hydrolysis of hemicellulosic fraction (110). The main benefits of using steam pretreatment are: (a) this technique no need to hazardous chemicals, (b) steam pretreatment has a low negative environmental impacts, and (c) it shows a high energy efficiency (111). In the other hand, steam pretreatment technique has two disadvantages: incomplete disruption of lignin and production of some toxic chemicals within the process. It seems that among physical pretreatment techniques for straw pretreatment, steam technique is the best chose since it partly hydrolyzes hemicellulose and enhance the enzymatic digestibility of cellulose remaining in biomass residues (112).

3.11 Liquid hot water

This technique applied hot water at high pressure to maintain its liquid form for degradation enhancement of the lignocellulosic matrix. Liquid hot water technique uses at temperature between 160 °C and 240 °C. Also, resident time in this technique is between few minutes and an hour. It was reported that 88% to 98% of xylose recovery can be obtained using liquid hot water without needing acid or chemical catalyst which make it an environmental friendly and cost-effective techniques for pretreatment of lignocellulosic biomasses (8). The disadvantage of this technique is high energy and water consumption.

3.12 Wet oxidation

Wet oxidation is a technique in which the lignocellulosic materials are treated with water and air or oxygen at temperatures more than 120 °C (113). The toxic furfuraldehydes and phenol aldehydes formation is reduced when alkali and wet oxidation is combined with each other (114). Since lignin and hemicellulose are solubilized, bagasse cellulose content increases within wet oxidation technique (115). A main difficulty in the fermentation of dilute acid hydrolyzates is the inability of the fermentative microorganism to withstand inhibitory compounds formed during pretreatment, and usually a detoxification step is needed to improve hydrolyzate fermentability (116). Similar results could also be obtained for fermentation of the rice hulls and wheat straw dilute acid hydrolyzates (117). The inhibitor problem can reduce when alkaline peroxide pretreatment was used for rice hulls. It was reported that combination of wet oxidation and base readily oxidizes lignin for wheat straw can facilitate the enzymatic hydrolysis of polysaccharides (114). Furfural and hydroxymethylfurfural were not generated within the wet oxidation technique. Carboxylic acids and dissolved hemicellulose can be directly used as nutrient source by fungal growth. It has been demonstrated that rice hull hemicellulose is able to be hydrolyzed using a single preparation of xylanase (viscosar) after a pretreatment alkaline peroxide (118).

3.14 Ammonia fiber explosion

The pretreatment of ammonia fiber explosion technique is approximately analogous to the steam explosion technique. In ammonia fiber explosion technique, lignocellulosic biomass is contacted to liquid ammonia at pressure from 250 to 300 psi and temperature between 60 and 100 °C during a period of time and then the pressure is quickly decreased. Several operational parameters such as number of treatments, resident time, the amount of pressure, water loading, temperature, and ammonia loading (119). This technique has many advantages including: (a) no toxic compounds are produced during the process, enhanced enzyme production (e.g., cellulase), and high surface area (40, 120). Additionally, this technique has an important disadvantage. It is not able to remove high amount of hemicelluloses that can increase the accessibility of enzyme and the yield of final sugar (40).

4 Conclusion and future recommendation

Although several different techniques such as microwaves, biological, alkaline, ionic liquid, organic solvent, acid, mechanical, pyrolysis, steam, wet oxidation, ammonia fiber explosion and liquid hot water have been developed for the biomass pretreatment, many obstacles are still needed to be overcome to use these techniques for industrial application. The surface area is the most important effective parameter on pretreatment process. It was demonstrated that single pretreatment technique is not able to obtain a very high performance for the biofuel production. Therefore, the studies must be focused on combined pretreatment techniques. Also, study on the energy consumption of pretreatment techniques and the feasibility of using such techniques is another necessary topic that should be intensively investigated. Certain corps can be efficiently pretreated using some particular pretreatment techniques due to their added advantage over others. Although lignin should be eliminated using pretreatment techniques for enhancement of biofuel production, recent studies show that lignin may be used in construction industry, dust particle controls, cleaning metallic surfaces, chemical coatings, agro farmland improvements, and paint industry.

Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors’ contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

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