J. Environ. Treat. Tech.
ISSN: 2309-1185

Journal weblink: http://www.jett.dormaj.com

A Critical Review on the Various Pretreatment Technologies of Lignocellulosic Materials

Amirreza Talaiekhozani[1], Shahabaldin Rezania[2]

[2] Department of Civil Engineering, Jami Institute of Technology, Isfahan, Iran
[1]Department of Environment and Energy, Sejong University, Seoul 05006, South Korea

Received: 12/01/2020 Accepted: 11/06/2020 Published: 20/09/2020

Abstract

Nowadays, finding new sources of renewable energy is an essential need for humans. The production of biofuel is a suitable way to find such a renewable energy source. Pretreatment is considered an important step for biofuel production. This study aimed 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 for the 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 a 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). The pretreatment process is the first stage for biomass conversion to biofuel. Many studies reported the importance of the pretreatment step on biofuel production processes (5). The well-known technique for biomass pretreatment is the thermochemical technique. These techniques are 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 abundant; therefore, these types of biomasses are attractive to be used as raw materials for biofuel production (6). Raw lignocellulosic biomass cannot easily be used for biofuel production due to the existence of some recalcitrant compounds and very complex structures (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 the 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 bio-oil, biodiesel, and biogas (5, 11-14). Bioethanol production is the most important way to produce energy from lignocellulosic 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 the selection of this type of biomass to produce different energy sources like bioethanol. Lignocellulosic biomass has a low amount of oil and that's why this type of biomass is not suitable for the production of biodiesel. Biogas is usually utilized for the generation of thermal or electrical energy and it is not used as a vehicle fuel. Biodiesel is another important technology of energy conversion. The transesterification process of animal fats and vegetable oils is a way to generate biodiesel. Biodiesel is mostly achieved from a specific type of plants such as rubber seed (15), coconut (10), mahua (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 does not have oils that are necessary for biodiesel generation. Although some crops such as mustard have oils they are used for animal feed. Fresh oil of vegetables has a viscosity between 28 and 40 mm^2/s. Direct usage of vegetable oil as a 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 requires a large amount of water to grow (20000–30000 m^3/ha); therefore, the 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 large amounts of air pollutants (25). Several inexpensive lignocellulosic agricultural wastes are accessible such as wheat straw, rice straw, softwood, switchgrass, salix, willow, timber species, rice hull, and sugarcane bagasse as a feedstock for biofuel production. In some countries that have 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. Lignocellulos 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-cellulose 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 cellobios 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).

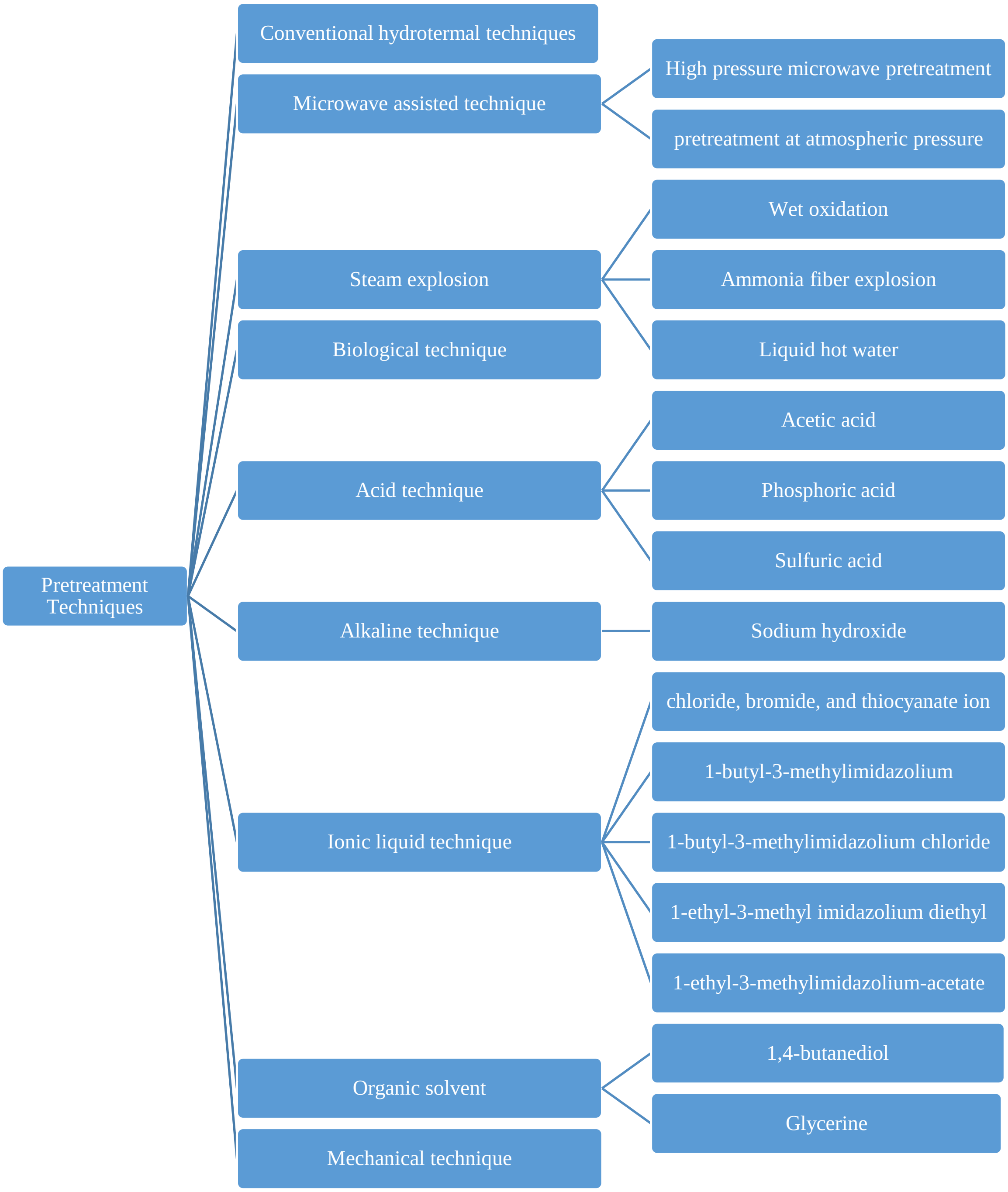

Figure 1: Categorization of pretreatment techniques (35)

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 a 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 lignocellulosic biomass is illustrated in Figure 2. Lignocellulosic biomass can be biologically or chemically degradable after the 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 the 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 step in biofuel production. It was reported that delignification has an intensive effect on all next steps in 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 the 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 the utilization of accessory enzymes including laccase and xylanases may decrease the concentrations of the enzymes required. It can also improve the cost-effectiveness of biofuels generation. The lignocellulosic 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 lignocellulosic biomass (except large chunks) has not a significant influence on the enzymatic digestibility of bagasse (10), switchgrass (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 the 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 lignocellulosic biomass. A microwave is an electromagnetic wave with a wavelength between radio waves and infrared radiation. Microwave radiation for pretreatment of lignocellulose 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 the microwave technique a promising technique for the pretreatment of lignocellulosic biomass. The conventional pretreatment techniques such as autohydrolysis, steam explosion, and diluted acid pretreatment must be done at high pressure and temperature. These pretreatment techniques can break complex chemical bonds of lignin-carbohydrate, lignin, and hemicellulose. In this condition, cellulose can be exposed to cellulase attacks. Usually, lignocellulosic biomasses 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 biomasses should be crushed into 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. The microwave technique can 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, 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).

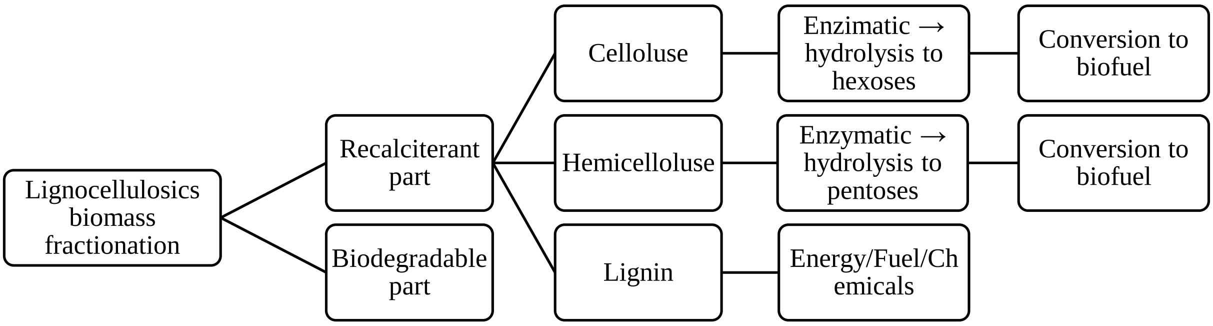

Figure 2: Fractionation of lignocellulosic biomasses (35)

Salt ions have more movement in the electric field compared with pure water; therefore, the heat of salt solution can increase faster to the expecting temperature. Studies on the pretreatment using the 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 conditions enzymatic hydrolysis ratio was 90.66%. Although a higher amount of calcium chloride can decrease the required temperature for pretreatment of corn stover, it was difficult to separate it from the solution after finishing the process (50). Pretreatment of lignocellulosic biomasses can be efficiently pretreated by acid (51). Microwaves can be used as a suitable alternative for increasing temperature in the 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 an atmospheric pressure microwave, the high-pressure microwave should be done in closed reactors. The range of temperature in this type of reactor is between 150 and 250℃. In the high-pressure microwave technique, higher temperatures can reduce the resident time and increase performance for pretreatment. Using the microwave pretreatment under high pressure requires a more complex reactor. A dynamic microwave pretreatment reactor was employed by (52). 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. The application of such a big liquid-solid ratio can increase the consumption of energy by a microwave reactor which reduces the economic viability of pretreatment (52). A continuous microwave reactor was designed for biomass pretreatment on 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 required 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℃) 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 an absorbing medium of the microwave to pretreat softwood by two groups of scientists (55, 56). They demonstrated that the ratio of hydrolysis of polysaccharides to soluble sugars was enhanced by 5.23% compared to that with conventional heating. Ferric sulfate was used for the pretreatment of bamboo using a microwave as a 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 the 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 other pretreatment techniques such as hydrothermal or acid. On the other hand, this technique needs a lower operation temperature but it requires a longer residence time (between hours and days). Generally, sodium hydroxide has been employed as a basic catalyst (58). In an alkaline pretreatment, sodium hydroxide solution was used to improve the generation of biogas from residues of the 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, the heating time of 22.50 min, and alkali concentration 2.75% (61). The 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 a heating time of 15 min, 10 Kg sodium hydroxide/m^3, 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 the attention of a large number of 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, bromide, and thiocyanate (63) reported that nearly 25% of cellulose was able to dissolve in 1-butyl-3-methylimidazolium when it was heated. An ionic liquid containing 1-ethyl-3-methylimidazolium-acetate, 1-ethyl-3-methyl imidazolium diethyl, 1-butyl-3-methylimidazolium chloride, and 1-allyl-3-methyl imidazolium-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, the viscosity of ionic liquids is gradually increased which 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-butanediol are usually applied for biomass pretreatment. Usage of high boiling organic solvents at a 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 the removal of lignin. During this process, the organic solvent can be recycled which is considered as an advantage of the organic solvent technique. Moretti et al. (2014) used different organic solvents (phosphoric acid, glycerol, and water) for the pretreatment of bagasse. They could found that this technique is more effective to hydrolyze sugarcane bagasse when glycerol was used as a 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 for high reducing sugars in this technique (65). It was reported that simultaneous usage of glycerine 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 parameter on pretreatment performance at more than 160˚C while it is not effective under lower than 100˚C. Three different solvents were applied by (66): alkaline glycerol, aqueous glycerol, and water as the 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 the 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 causes a dramatic change in its structure. These results illustrated that the type of organic solvent should be selected based on the 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, lignocellulosic 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 conditions could convert hemicelluloses into soluble sugar; therefore, the cellulose could be simply degraded due to changes in the structure of biomass. Increasing 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 the surge was converted (51). Starch-free wheat fibers were pretreated in a low concentration of sulfuric acid (71). They found that using the microwave as a heating source is more effective than steam for the acid pretreatment. The effects of temperature on the structure of lignocellulosic biomasses with 0.2 M sulfuric acid were studied (72). They showed that the increase in 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 the 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 the pretreatment of lignocellulosic biomasses. It is reported that up to 100% of hemicellulose can be eliminated when the acid technique is used (74). The plant cell wall contains two important compounds: hemicellulose and lignin. These compounds have been linked by three main co-valent bonds for the formation of lignin–carbohydrate complexes (75). Lignin–carbohydrate complexes are considered recalcitrant compounds in lignocellulosic biomass. The degradation of hemicellulose causes rearrangement of the lignin molecular structure. In this case, cellulose is exposed by cellulase enzyme; therefore, the rate and proportion of cellulose degradation will be enhanced (76). The presence of sulfur oxide shows some particular advantages as a hydrolysis catalyst over sulfuric acid. Sulfur dioxide can be added either with the steam or ahead of the reactor. It is better to 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 the presence 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 environmentally friendly technique for the pretreatment of biomass. Value-added products may be produced during biological pretreatment of lignocellulosic biomasses which makes it an economic technique. Biological pretreatment of lignocellulosic biomasses can 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 sustainability during the generation of biofuels. This combination showed an environmentally friendly and cost-effective way to produce biofuel (84). Although the technique of biological pretreatment has the 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 promising results compared to the results achieved from using biomass without pretreatment (86, 87). Although the number of studies on biological pretreatment of lignocellulos 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). Lignocellulose has a high quantity of lignin in their cell walls while microalgae have protein, lipid, and starch, without any lignin (89). Sometimes lignocellulose 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 the pretreatment of microalgae (91, 92). The reasons for the 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 an anaerobic reactor goal 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 on large scale; therefore, more studies should be done to collect this technical information.

3.8 Mechanical techniques

Several kinds of techniques are introduced to reduce the size of lignocellulosic biomass including milling, grinding, shredding, and chipping for increasing its digestibility (95). Mechanical pretreatment techniques 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 a size of between 10 and 30 mm. Grinding and milling have better performance and they can produce materials with a 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 ligniocellulosic biomasses such as hardwoods is higher than agricultural wastes (97). Although some reports show that 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 pieces of research 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 show that vibratory ball milling is a more effective technique compared to the ball milling technique to decrease the cellulose crystallinity of aspen and spruce chips (10). Also, disk milling that can 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 the pyrolysis technique. Cellulose can be decomposed into residual char and several gaseous products at a temperature of more than 300℃. it should be noted that the rate of cellulose decomposition at temperatures less than 300℃ 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 the 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℃. Several reports showed that pretreatment using steam can hydrolyze the hemicelluloses and modify the lignin. It can also enhance the surface area and reduce the degree of polymerization and cellulose crystallinity (103). Corn stover pretreatment using steam with and without sulfur dioxide was studied by (74). There are some reports to show that the existence of few amounts 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% 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 the 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 the depressurization step, the size of biomass particle is reduced which increases the cellulose enzymatic accessibility. It was reported that steam pretreatment is an efficient technique for corn stover biomass (109). Steam pretreatment can efficiently break down the lignocellulosic structure, defibration, depolymerization of the lignin components, and hydrolysis of the hemicellulosic fraction (110). The main benefits of using steam pretreatment are: (a) this technique no need for hazardous chemicals, (b) steam pretreatment has low negative environmental impacts, and (c) it shows a high energy efficiency (111). On the other hand, the 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, the steam technique is the best choice since it partly hydrolyzes hemicellulose and enhances 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. The liquid hot water technique uses at a 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 makes it an environmentally friendly and cost-effective technique 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 formaldehyde and phenol aldehydes formation is reduced when alkali and wet oxidation is combined with each other (114). Since lignin and hemicellulose are solubilized, baggase 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 (viscostar) after a pretreatment alkaline peroxide (118).

3.14 Ammonia fiber explosion

The pretreatment of the ammonia fiber explosion technique is approximately analogous to the steam explosion technique. In the 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 and then the pressure is quickly decreased. Several operational parameters such as the 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 a high amount of hemicelluloses that can increase the accessibility of enzymes 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 in the pretreatment process. It was demonstrated that a single pretreatment technique is not able to obtain very high performance for biofuel production. Therefore, the studies must be focused on combined pretreatment techniques. Also, the 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 the construction industry, dust particle controls, cleaning metallic surfaces, chemical coatings, agro farmland improvements, and the paint industry.

Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically concerning 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 no conflict of interest would prejudice the impartiality of this scientific work.

Authors’ contribution

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

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