Current Progress on Biomass Pretreatment: The Key for Its Valorization

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Abstract It has become a global concern for reducing the utilization of fossil sources for energy and chemical purposes. Not only environmental issues such as greenhouses gases increment but also depleting fossil reserves, which became the reason to quest for new and renewable raw materials. Lignocellulosic biomass that is abundantly available is being studied as a potential material to provide both fuels and biochemicals. However, to fractionate and disintegrate its main components: cellulose; hemicellulose and lignin is a very challenging step. Different pretreatment approaches that considering energy consumption, cost effectiveness, percentage of lignin removal, further utilization of the cellulose, hemicellulose, lignin, and environmentally friendly process have been applied. The review covers the recent pretreatment technology that applied physicochemical approach; chemicals pretreatment and application of Deep Eutectic Solvent (DES); biological pretreatment; and high energy of radiation. This study explained a deeper understanding of the pretreatment technologies for developing biorefinery concepts to support the sustainable development of utilization of lignocellulosic biomass.

Keywords Lignocellulosic · Pretreatment · Physicochemical treatment · Biological pretreatment

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M. A. R. Lubis et al. (eds.), *Biomass Conversion and Sustainable Biorefinery*, Green Energy and Technology, https://doi.org/10.1007/978-981-99-7769-7_1

1 Introduction

Pretreatment of lignocellulosic biomass is the key for the separation of cellulose, hemicellulose, and lignin. Several factors such as the energy required and the economical value of the biomass pretreatment will be the key for industrial application. Another consideration is the end product of the fractionation. For instance, lower molecular weight or lower density cellulose will not be suitable for dissolving pulp application. Moreover, the enzymatic accessibility will be the key factor for the saccharification of cellulose into the sugar on the bioethanol production process.

The main objective of the pretreatment process on lignocellulosic biomass is lignin removal. Determination of the pretreatment methods depends on the type of lignocellulosic biomass. Therefore, no universal pretreatment can be applied to all lignocellulosic biomass (Costa Sousa et al. 2009). Therefore, it can be summarized that pretreatment has to be: (a) considering energy consumption, (b) cost-effectiveness, (c) percentage of lignin removal, (d) further utilization of the cellulose, hemicellulose, lignin, and (e) environmentally friendly process.

Generally, the pretreatment of biomass can be divided into chemical, physical, biological, physicochemical, and high-energy radiation treatment. However, combination of these methods is mostly applied to get desirable results. This study aims to provide recent information and discuss the above-mentioned biomass pretreatment methods as the information for choosing suitable pretreatment conditions to get optimum fractionation for wood and non-wood biomass components.

2 Pretreatment Methods

2.1 Physicochemical Pretreatment

Physicochemical pretreatment is believed to cause more well lignin removal and cellulose crystallinity decrement efficiency as compared with physical, chemical, and biological pretreatment (Zhao, et al. 2021). The most widely used physicochemical pretreatment involved liquid-hot water (LHW), steam explosion, alkali explosion or alkali-heat pretreatment, and ammonia fiber expansion (AFEX) (Wang et al. 2015; Elliston et al. 2015; Jacquet et al. 2015; Yu et al. 2022; Sudiyani et al. 2020; Nurani et al. 2020; Emam 2013; Chundawat 2020; Bensah and Mensah 2018).

2.2 Liquid-Hot Water (LHW) Pretreatment

Liquid-hot water (LHW) is one of the pretreatment technologies utilizing liquid water without other chemicals at high temperature and pressure (Yan et al. 2016; Zhuang et al. 2016). Water serves as a solvent and also a catalyst accompanied

by removed organic acids from biomass to aid in disrupting the cell wall matrix (Mosier 2013). Moreover, LHW brings increased cellulose accessibility and produces minimal inhibitory products (Kim et al. 2009). After LHW pretreatment, the major changes in lignocellulose involve the limited deconstruction of cellulose, dissolution of hemicellulose, partial removal of lignin, and carbohydrate degradation. Nitsos et al. has been demonstrated that hemicellulose is almost completely solubilized and deconstructed from biomass in hot water pretreatment at ~200 °C for 50 min (Nitsos et al. 2016). Different from hemicellulose, cellulose was less affected by LHW pretreatment. Less than 22% by weight of cellulose is degraded in wood and herbaceous biomass treated with LHW at 200–230 °C (Mok and Antal 1992).

2.2.1 Steam Explosion

Steam explosion is an effective, environmentally safe, and industrially scalable pretreatment method. This pretreatment results in the combination of structural disruption of biomass by high-temperature steaming and explosive decompression as well as autohydrolysis (Singh et al. 2015; Kumari and Singh 2018). Generally, steam explosion was carried out under high-pressure steam (0.5–5 MPa) and temperature intervals between 160 and 250 °C (Paudel et al. 2017). This method uses less chemicals and does not result in unnecessary dilution of hydrolyzates, but the steam explosion has some disadvantages, such as energy intense, inhibitory compounds generation, and causing the partial ruin of carbohydrate-lignin matrix (Agbor et al. 2011). To improve the effectiveness of the steam explosion method, the addition of a catalyst or impregnating agent such as H_2SO_4, SO_2, or CO_2 can decrease the production of inhibitors and improve the enzymatic hydrolysis on the biomass (Mosier et al. 2005; Sun and Cheng 2002).

The most attractive catalyst is CO_2 due to its cheap cost of CO_2, low corrosion, low toxicity, and the possibility of biomass having high solids content (Kucharska et al. 2018). In most cases, CO_2 explosion applies supercritical CO_2 or high-pressure CO_2 to help the biomass digestibility (Zheng et al. 1998; Morais et al. 2015; Hendriks and Zeeman 2009). Moreover, adding CO_2 in mild condition before steam explosion pretreatment also has been studied can increase the surface area of the material which can make the enzymes more easily to enter the material during the hydrolysis process. Pretreatment of oil palm empty fruit bunch (EFB) using steam explosion with CO_2 as an impregnating agent gives more slightly lower crystallinity index, more disrupt biomass, and increasing enzymatic hydrolysis of EFB as compared to pretreatment EFB using conventional steam explosion (Triwahyuni et al. 2021). The changes in the surface morphology of EFB using SEM results in the untreated EFB fiber had a rigid surface, with a layer of matrix material, meanwhile, the surface of EFB after CO_2-added steam explosion, appeared uniform pores in the surface of EFB. It indicated that some silica was removed from EFB (Triwahyuni et al. 2021).

2.2.2 Alkali Explosion

Alkali explosion is one of chemical pretreatment which can provide a high yield of delignification. Alkali-heat pretreatment uses heat and the alkali such as sodium hydroxide, sodium carbonate, and alkaline peroxide to dissolve lignin and reduce the crystallinity of lignocellulose by swelling, and also enlarge the specific surface area of cellulose (Rodrigues et al. 2016). For example, the delignification of EFB using NaOH explosion reached 58.36% and the percentage of cellulose could increase from 30.16% (untreated EFB) to 63.82% (Muryanto et al. 2015). Pretreatment of corn straw with NaOH-heat pretreatment obtained lignin and hemicellulose removal efficiency of 54.09% and 67.67%, meanwhile, the relative content of cellulose enhanced to 51.65% (Zhao, et al. 2021; Lopez et al. 2019; Shahabazuddin et al. 2018). The ability of NaOH to dissolve lignin is due to the opening of aromatic rings of lignin caused by the use of high temperatures and pressure, then, the resulting explosive effects can dissolve these components (Rezania et al. 2020). However, this method requires high temperature and pressure and takes a long time as well as high treatment cost (Muryanto et al. 2015; Kumar et al. 2020).

2.2.3 Ammonia Fiber Explosion

Ammonia fiber explosion is one of physicochemical pretreatment under high pressure with ammonia and oxyhydrogen ions released from liquid ammonia, resulting in a prompt rise in temperature and breaking the ester bond and ether bond between hemicellulose lignin in lignocellulose (Zhao et al. 2020) as well as reducing the cellulose crystal. AFEX has been demonstrated to be effective in low lignin-contained lignocellulose pretreatment. The application of AFEX shows lignin degradability of barley straw (Beauchemin et al. 2019) and corn stover (Mankar et al. 2021) achieved 24–1.3%.

2.2.4 Chemi-Extrusion Method

Application of the combination of alkaline and thermochemical can reduce energy consumption and remove lignin (Chen et al. 2019). However, these combinations still cannot meet the requirements for industrial scale that need efficient operational cost. The extrusion method then be considered as one of the solutions because it applies both chemical and physical methods. Moreover, in the biomass processing temperature can be applied together with compression forces.

Extruder screws are used in the extrusion method and the single or twin screws are usually used. The screws rotate to generate shear forces, an unaligned force acting on one part of a reactor in a particular direction, among the biomass, screw, and barrel. These forces generally increase the temperature and the pressure inside the reactor which will change the biomass's physical properties. It has been studied that shear force will strengthen the rotation of biomass, the screw, and the barrel. Pressure

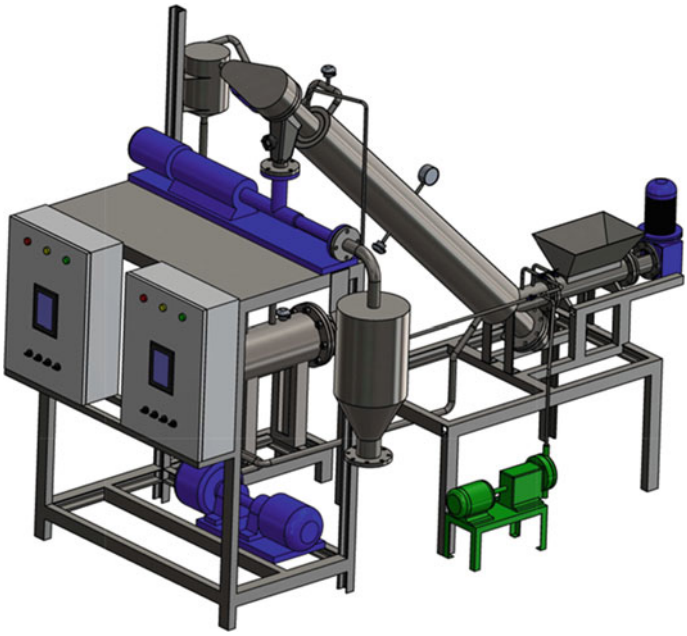

Fig. 1 Screw continuous reactor model that has been installed at research center for chemistry—BRIN

and temperature increased during the process will lead to the breakage of biomass lignocellulosic fibers (Khan et al. 2021).

It has been reported that screw rotation speed, residence time in the screw reactor, and temperature influenced the lignin removal percentage by using 10% NaOH (Maryana et al. 2022) (Fig. 1).

Moreover, screw speed is responsible for the reduction of the length of fiber and increasing of the surface area of biomass that improve sugar yield after the saccharification process (Karunanithy and Muthukumarappan 2010). The screw extrusion method is usually combined with chemical and thermo-chemical methods. The second generation of bioethanol production has used the extrusion method. For instance, the application of a single screw extruder that used a corn stover by varying different screw speeds and temperatures (Karunanithy and Muthukumarappan 2010; Jorge et al. 2006).

2.3 Chemicals Pretreatment and Application of Deep Eutectic Solvent (DES)

2.3.1 Chemicals Pretreatment

Chemical pretreatment is generally divided into alkaline and acid pretreatment. Alkaline pretreatment can use NaOH, $Ca(OH)_2$, KOH, or alkaline peroxide, a combination of NaOH and H_2O_2 (Alvarez-vasco and Zhang 2013). The mechanism of alkaline pretreatment is the saponification of intermolecular ester bonds that cross-link silane and other components (Sun and Cheng 2002). However, alkaline pretreatment has some disadvantages, such as longer time pretreatment, more water for biomass washing, and more expensive waste recovery costs (Rezania et al. 2017). Acid pretreatment uses low concentrations of mineral acids such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl). Sometimes concentrated acid can be used to conduct pretreatment at low temperatures. Acid pretreatment commonly hydrolyzes cellulose and hemicellulose to get monomeric sugar that can be converted to some biobased chemical. Produce inhibitor products, hard to separate, and corrosive are the disadvantages of acid pretreatment. Therefore, many studies have been conducted to develop green solvents in the delignification process. The ionic liquid is widely developed because it is environmentally friendly compared to conventional solvents (Nguyen et al. Oct. 2010; Pena-Pereira and Namieśnik 2014). However, the ionic liquid is still as expensive as solvent pretreatment.

2.3.2 Deep Eutectic Solvent (DES)

Deep eutectic solvent (DES) has been introduced as the new green solvent (Abbott et al. 2001). DES is a solvent consisting of a mixture of a high melting point salt (i.e., hydrogen bond acceptor or HBA) with a molecular hydrogen bond donor (HBD) in a specific ratio to form a liquid. DES has properties like an ionic liquid, although the DES ion content is lower. DES began to be used in the pretreatment process because of several advantages such as cheaper material costs, non-toxicity, ease of manufacturing process, and more biodegradable and biocompatible (Haldar and Purkait 2021). Besides that, most DES have high solubility for lignin and poor solubility for cellulose and hemicellulose (Francisco et al. 2012). DES can be explicitly made according to the required properties that are needed in the process. Table 1 shows the DES from a variation of HBD and HBA.

DES in the pretreatment process is divided into several types depending on the HBD used. Several types of DES include carbohydrate-based DES, such as CHCl-glucose and CHCl fructose. Polyalcohol-based DES consisted of CHCl-glycerol, CHCl-ethylene glycol, and CHCl-Propanediol. Acidic DES is commonly used in biomass processing, containing HBD such as acetic acid, lactic acid, glycolic acid, oxalic acid, and citric acid. Basic-based DES contains amide, amine, and imidazole

Table 1 Deep Eutectic solvent in the variation of HBA and HBD

HBA	HBD	Ratio HBA:HBD	Molar masses (kg/mol)	T melting point (°C)
Choline chloride	Urea	1:2	0.2597	12
	Malonic acid	1:1	0.24368	10
	Lactic acid	1:2	0.31978	−78
	Oxalic acid dehydrate	1:1	0.26569	−40
	Ethylene glycol	1:2	0.26376	−66
	Glucose	2:1	0.43237	15
Choline acetate	Urea	1:2	0.27168	<−20
Choline fluoride	Urea	1:2	0.24329	1
Acetylcholine$^{+}Cl^{-}$	Urea	1:2	0.26627	−14
	Glucose	1:1	0.36382	−7
Proline	Oxalic acid	1:1	–	−14.5
	Lactic acid	2:1	–	−36.7
Betaine	Urea	1:2	–	−42.5
	Oxalic acid	1:1	–	−17.2
	Lactic acid	2:1	–	−46.9
Glucose	Citric acid	1:1	–	9.8
	Tartaric acid	1:1	–	−18.3
$AlCl_3$	Urea	1:1	–	<25
K_2CO_3	Ethylene glycol	1:10	–	−122

Source Marcus and Solvents (2019)

compounds. CHCl-Urea is a basic DES commonly used in biomass processing (Tan et al. 2019).

The pretreatment performance may be impacted by pretreatment parameters, including temperature, duration, or the solid-to-liquid ratio, and DES type also affects DES pretreatment. For example, DES Pretreatment conducted by Majová et al. (2017) used hardwood kraft pulps as raw materials and DES solution from a mixture of ChCl-Oxalic Acid with a 1:1 molar ratio (Majová et al. 2017). The pretreatment process was carried out for 1 h at a temperature of 60 °C. The results obtained from DES pretreatment were able to degrade lignin in hardwood kappa pulp by 38.7%. Another study conducted by Okur and Koyuncu (2020) regarding the delignification of rice husks using a DES solution of ethylene glycol-citric acid obtained optimal results at a temperature of 120 °C and a processing time of 4 h showed that 57.33% of lignin was degraded (Okur and Koyuncu 2020). DES pretreatment consisting of K_2CO_3 and glycerol was conducted on wheat straw and corn stalks at a temperature of 80–100 C for 8–24 h. This pretreatment can reduce the lignin content in wheat straw and corn

Table 2 DES pretreatment

DES	Molar ratio	Biomass	Process condition	Delignification (%)	Sources
CHCl:ethylene glycol	1:2	Switchgrass	130 °C, 30 min, S/L 10	24	Chen and Wan (2018)
CHCl:glycerol	1:2	Oil palm trunk	100 °C, S/L 5	49	Zulkefli et al. (2017)
CHCh:lactic acid		Poplar wood	145 °C, 9 h, S/L 10	79	Alvarez-Vasco et al. (2016)
CHCl:lactic acid	1:5	OPEFB	120 °C, 8 h, S/L 10	88	Tan et al. (2018)
CHCl:formic acid	1:2	Akebia herbal residue	120 °C, 8 h, S/L 10	41	Yu et al. (2018)
CHCl:urea	1:2	OPEFB	120 °C, 8 h, S/L 10	34	Tan et al. (2018)
CHCl: monoethanolamine	1:6	Wheat straw	90 °C, 5 h, S/L 5	81	Zhao et al. (2018)
CHCl:4-catechol	1:1	Switchgrass	160 °C, 3 h, S/L 5	49	Kim et al. (2018)

stalks from 22% to 12.1% and 24% to 16.3%, respectively (Suopajärvi et al. 2020). DES pretreatment in variation DES type and operation condition is shown in Table 2.

DES is used in the pretreatment process in various delignifications. Some types of DES can reduce the lignin content above 60%. However, some are still low. Like the chemical pretreatment process, DES pretreatment can also be combined with other technologies to improve its performance. Some integrations can include combining microwave, ultrasonic, and sequential pretreatment with hydrothermal, biological, or another chemical (Tan et al. 2019).

2.3.3 Organosolv Pretreatment

Organic solvents such as methanol, ethanol, acetone, ethylene glycol, and tetrahydrofurfuryl alcohol are commonly used as pretreatment chemicals in the organosolv method. Moreover, catalysts like salicylic acid and organic acid as well as sodium hydroxide are generally used in this method (Cheah et al. 2020). It was reported by Mirmohamadsadeghi et al., that pretreated Elmwood, pinewood, and rice straw resulted in lignin removal of 27, 21, and 37.7% respectively, after pretreated by using 1% (w/w) sulfuric acid at 150–180 °C for 30–60 min in 75% aqueous ethanol (Mirmohamadsadeghi et al. 2014).

Ethanol is the most common solvent due to its economical price, not harmful properties, ease of mixing with water, and good soluble solvent for lignin. In the case of softwood delignification, ethanol can enhance the impregnation and support lignin fragments in the biomass to the liquor solution (Rinaldi et al. 2016). It was

studied that lignin removal of 16 for 50% water–ethanol system at 175 °C for southern yellow pine that was pretreated for 80 min (McGEE and APRIL 1982).

2.4 Biological Pretreatment

The effectiveness of a biological pretreatment is determined by several factors including composition of biomass, moisture content, incubation time, temperature, pH, and type of microorganism (Sindhu et al. 2016). Based on the composition of biomass, a suitable microbial consortium must be used for the effective removal of lignin and hemicellulose from the biomass.

2.4.1 Microorganism Used in Biological Pretreatment

Many researcher-published articles revealed that common microorganisms used in biological pretreatment are bacteria including *Bacillus*, Actinomycetes and some known fungi are able to degrade organic matter (Poszytek et al. 2016). Microbial consortia consisting of cellulolytic bacteria of the genus *Bacillus, Streptomyces, Candida*, and *Aspergillus* exhibit broad-spectrum biodegradation. It was also that many potent brown rot fungus, white rot fungus, and softening fungi. Among the three fungi, the most effective for upstream treatment of lignocellulosic materials is white rot fungi. The white rot fungus helps in delignification which in turn improves the enzymatic saccharification rate, especially, *Phanerochaete chrysosporium*, *Ceriporiopsis subvermispora, Pleurotus ostreaus, Ceriporia lanceolata* and *Cyanthus stercoreus*, which selectively degrading lignin by producing a wide variety of enzyme, i.e., laccase, lignin peroxidase (LiP), and manganese peroxidase (MnP) (Maurya et al. 2015).

Currently, there is a need for unique consortia for biological pretreatment. Effective biodegradation of lignocellulosic biomass takes place by biodegradation by synergistic action of microbial consortiums including various bacteria and fungi. There are several advantages of using microbial consortium which include increased adaptability, improved productivity, improved enzymatic saccharification efficiency, control of pH during sugar utilization, and increased substrate utilization (Kalyani et al. 2013).

The development of an eco-friendly simultaneous pretreatment and saccharification (SPS) methodology using a cocktail of hydrolytic and oxidizing enzymes from a fungal consortium was reported by Dhiman et al., 2015 (Dhiman et al. 2015). The novel laccase effectively functioned as a detoxifying agent. This process completely eliminates the use of hazardous chemicals. Pretreatment and saccharification conducted in the same vessel make the process economically viable, reduce energy consumption, and generate a simple process for the removal of residual biomass.

Table 3 Microorganism used in the biological pretreatment

Microorganism	Biomass	Major effects
Punctualaria sp. TUFC20056	Bamboo culms for bioethanol production	50% of lignin removal
Irpex lacteus	Corn stalks	82% of hydrolysis yield, 28 days pretreatment
Fungal consortium	Straw	Seven-fold increase in hydrolysis
Pleurotus ostreatus/P. pulmonarius	Eucalyptus grandis saw dust	Twenty-fold increase in hydrolysis
Phanerochete chrysosporium	Rice husk	Cellulase, xylanase, lignin peroxidase, glyoxidase, and aryl alcohol oxidase were produced during 18 days pretreament
Fungal consortium	Corn stover	43.8% lignin removal/ seven-fold increase in hydrolysis
Ceriporiopsis subvermispora	Wheat straw	Minimal cellulose loss and highest sugar yield up to 44% after 10 weeks
Ceriporiopsis subvermispora	Corn stover	2–threefold increase in reducing sugar yield
Fungal consortium	Plant biomass	Complete elimination of the use of hazardous chemicals

Different biological pretreatment strategies are involved in the pretreatment of lignocellulosic biomass and its advantages (Sindhu et al. 2016) (Table 3).

Biological pretreatment is considered as an inexpensive process when compared to other pretreatment processes such as AFEX and organo solvent. Large-scale operation leads to high operational costs since pretreatment is to be carried out in sterile conditions and this increases the cost of the process. One approach to reducing the pretreatment time is by applying a combination of biological processes with physical and chemical methods. Employing more potent microbial consortia as well as the development of specific reactors for biological pretreatment can reduce the pretreatment time as well as the loss of carbohydrate significantly.

2.5 Pretreatment of Biomass with High Energy of Radiation

In order to produce a digestible raw material and prevent the target material from degrading and the production of harmful by-products, an efficient pretreatment should break down the lignocellulose structure. To enhance the available surface area and the size of pores in lignocellulosic materials, cellulose is physically separated by removing lignin and hemicellulose as well as breaking down the crystallinity

of the substance. Any pretreatment must be economically advantageous (Maryana et al. 2014, 2017, 2020).

Among other physical methods, high-energy radiation is regarded as an attractive method for the pretreatment process of biomass (Duarte et al. 2012; Khan et al. 2006; Mohd Asyraf Kassim et al. 2016). In general, radiation processing technology onto lignocellulosic material is defined as a radiolysis reaction that induces lignocellulosic material breakdown using radioisotopes like cobalt-60 (Co-60) or cesium-137 (Cs-137), or an electron beam generated by an electron accelerator. Generally, biomass materials degrade similarly under gamma and electron beam irradiation. As electromagnetic radiation, an electron beam has a significantly lower penetration but with a higher dose rate compared to gamma rays. The wide application of electron beams to the degradation of biomass is due to a number of its inherent benefits. Since electron particle energy is immediately transferred to molecules of biomass, thus no need for heating and catalyst during the irradiation. Because the electron beam can be precisely controlled by adjusting the accelerator's operating condition, the irradiation process by using EBM is highly reproducible, controllable, and precise.

High energy radiation from electron beams, X-rays, or gamma rays can create ions and/or radicals that initiate chemical processes that primarily cause chemical bond cleavages and decrease the molecular weight of the biomass by increasing the irradiation dose. The high-energy radiation produced during this process has the potential to change the properties of cellulosic biomass, due to 1,4-glycosidic linkages being ruptured by gamma radiation and electron beams. Subsequently increasing the lignocellulosic biomass' specific surface area, decreasing the polymerization and crystallinity of cellulose, hydrolyzing hemicellulose, and partially depolymerizing lignin (Al-Masri and Zarkawi 1994). The irradiation of biomass with an electron beam causes the complex carbohydrates to become soluble, which facilitates processing, such as enzymatic hydrolysis for the production of bioethanol (Danu et al. 2012).

The effectiveness of high-energy radiation as a pretreatment technique on lignocellulosic material has been studied intensively (Hyun Hong, et al. 2014). Irradiation of Jute fibers by gamma irradiation with the doses up to 100 kGy and by an electron beam with a dose up to 400 kGy for oil palm empty fruit bunch (OPEFB) resulted in a decrease in the weight fraction of large particles and an increase in the weight fraction of small and medium particles both of Jute fibers and OPEFB (Khan et al. 2006; Danu et al. 2012). It was revealed that the chemical stability of irradiated fibers gradually decreased with an increase in irradiation dose. Studies using thermogravimetry and differential scanning calorimetry revealed a considerable loss in thermal stability. The wide-angle X-ray diffraction analysis revealed that lignocellulose's chemical response to radiation caused structural alterations in cellulose. The solubility of irradiated OPEFB in water and 1% sodium hydroxide solution also increases. Based on the bands shown in the fingerprint area and the degradation found using FTIR analysis, cellulose, hemicelluloses, and lignin were identified as the primary constituents of OPEFB and were subject to C–O stretching and C–H deformation (Danu et al. 2012).

Combining irradiation with additional pretreatment techniques, both physical and chemical, can improve the effectiveness of gamma pretreatment. Pretreatment is more effective in relatively milder conditions when multiple treatments are used because they increase each other's effects (Duarte et al. 2012; Wang et al. 2012; Abo-State et al. 2014; Chung et al. 2012; Saini et al. 2015). The yield of total reducing sugar following saccharification and pretreatment of rice straw during the production of ethanol was enhanced by combining milling, autoclaving, and gamma irradiation (700 kGy) (Abo-State et al. 2014). When sugarcane bagasse was pretreated by using electron beam processing (EBP), after 24 and 48 h of incubation, the conversion yield of cellulose to glucose improved from 8 to 12% becoming 15%. The yield of the enzymatic hydrolysis of cellulose improved with EBP and thermal treatment (60 min at 180 °C), reaching 71.55%. After EBP, hemicelluloses were completely hydrolyzed (Kucharska et al. 2018).

The effect of gamma irradiation on the saccharification of Undaria sp. for bioethanol production was evaluated by Yoon et al. (2012). The irradiation has been employed as a pretreatment in conjunction with dilute acid hydrolysis. Undaria sp. wet samples were exposed to radiation at 22 °C with irradiation dose between 10 and 500 kGy and a dose rate of 10 kGy/h. By increasing the gamma irradiation dose, the concentration of reducing sugars increased. The reducing sugar content was 0.017 g/L for unirradiated samples, but it rose to 0.048 g/L for a sample irradiated by the dose of 500 kGy. This reveals that the combined method of gamma irradiation and diluted acid hydrolysis considerably enhances the saccharification process for the generation of bioethanol from materials derived from marine algae.

To improve enzymatic hydrolysis for the manufacture of bioethanol, poplar bark was pretreated with 3% w/w sulfuric acid and gamma radiation (0–1000 kGy). With an increasing irradiation dose, the yields of reducing sugar were slightly increased, going from 35.4 to 51.5%. After pretreatment by the addition of dilute acid, the yield of reducing sugar reached 56.1%. These results clearly demonstrated that soluble sugars were released more quickly and to a higher amount in poplar bark that had been prepared with diluted acid as opposed to bark that had been exposed to gamma radiation. A significant increase in reduced sugar yield (83.1%) was found after combination pretreatment as compared to individual pretreatment, suggesting that the convertibility of poplar bark may be improved after combined pretreatment (Chung et al. 2012).

On the other hand, Henniges et al. (2013) found that tuning the irradiation process, independent of the dosage, is possible to increase oxidation by introducing iron(II) ions. They observed the same amount of oxidized cellulose functionalities at better preservation of molar mass (less cellulose chain degradation). They found that the addition of hydrogen peroxide speeds up the irradiation-induced degradation. Another finding is that wet irradiation samples are more impacted than dry irradiated samples. When wet straw was utilized instead of dry straw, the required dose of gamma irradiation was decreased from 500 to 10 kGy.

According to some studies and reports, irradiating biomass for pretreatment uses less energy than other methods (Mosier et al. 2005; Mohd Asyraf Kassim et al. 2016; Henniges et al. 2013). This method is more effective and efficient for producing the

intended product since it is selective and easy to control. On the other hand, there are certain points that require to be considered due to the studies conducted in recent years only focusing on biomass irradiation at a lab scale. Meanwhile, validating the result requires pilot-scale investigations, and the cost of the commercial deployment must be investigated throughout technology development (Saini et al. 2015).

3 Conclusion

The Biorefinery concept is a potential approach to respond to the depletion of fossil resources by utilizing lignocellulosic biomass. Eco-friendly and efficient biomass pretreatment methods in order to fractionate cellulose, hemicellulose, and lignin are continuously developed. By studying several recent pretreatment methods, it can be concluded that the process has to overcome the recalcitrant of lignin in the chemical bonding complex with cellulose and hemicellulose. The cellulose crystallinity and sugars recovery are also the main concern of the pretreatment methods. Different pretreatment approaches that considering energy consumption, cost-effectiveness, percentage of lignin removal, further utilization of the cellulose, hemicellulose, lignin, and environmentally friendly process can be chosen for addressing the challenges in the biomass pretreatment method.

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