Toward Sustainable Processes of Pretreatment Technologies of Lignocellulosic Biomass for Enzymatic Production of Biofuels and Chemicals: A Review

Saleem Ethaib,[a,b,*] Rozita Omar,[a] Mustapa Kamal Siti Mazlina,[c] Awang Biak Dayang Radiah,[a] and Salah L. Zubaidi [d]

Lignocellulosic biomass is a class of sustainable material that can be utilized as a raw feedstock in biofuel and chemical production. However, the complex matrix structure of lignocellulosic materials complicates conversion processes, such as enzymatic hydrolysis. Therefore, an efficient pretreatment process is required to disrupt the plant cell wall structure and maximize the recovery of valuable soluble components from lignocellulosic biomass during hydrolysis. In addition, an effective pretreatment method should use the minimum necessary amounts of energy and chemicals to minimize the cost of the end product. Further, it should reduce the formation of inhibitory compounds that affect enzymes and microorganisms during hydrolysis and fermentation, and it should be applicable to a wide variety of feedstocks. The research presented in this review has highlighted the pros and cons of the current technologies employed in pretreatment processes. Further study should be done to optimize and improve these technologies to enhance the efficiency of the production of biofuels and other valuable components.

Keywords: Pretreatment; Lignocellulosic biomass; Enzymatic hydrolysis; Monomeric sugar

Contact information: a: Department of Chemical and Environmental Engineering, Faculty of Engineering, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia; b: College of Engineering, University of Thi-Qar, 64001 Al-Nassiriya, Iraq; c: Department of Process and Food Engineering, Faculty of Engineering, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia; d: Department of Civil Engineering, College of Engineering, Wasit University, Iraq;
** Corresponding author: salem_eidt@yahoo.com*

INTRODUCTION

Recently, the sustainable production of energy, fuel, pharmaceutical, and nutraceutical products has become an issue of global attention. Population growth, climate change, and the depletion of fossil fuel reserves have caused concern about the environment, energy, and food security (Owusu and Asumadu-Sarkodie 2016). Researchers have focused on the use of renewable and affordable natural sources in various industrial applications (Rahimi *et al*. 2017; Mokhtar *et al*. 2018; Maktoof *et al*. 2020). Lignocellulosic biomass is a renewable natural resource, and it is the most abundant and widely available biopolymer on earth (Ingle *et al*. 2020). The annual global yield of lignocellulosic biomass, including agricultural, agro-industrial, and forestry residues, is approximately 100 million to 500 million dry tons, which constitutes approximately half of the total global production of biomass (Ibraheem and Ndimba 2013). In addition to its availability in enormous quantities at low cost, lignocellulosic biomass has a high carbohydrate content. These reasons have encouraged the use of lignocellulosic materials

as a unique and sustainable resource for sugar-platform-based organic fuels and chemicals (Ethaib *et al.* 2020a).

The development of alternative feedstocks using lignocellulosic biomass as a raw material for energy, food, and pharmaceutical components requires the management of several obstacles. The structural contents of lignocellulosic biomass consist of long cellulose fibres that are held together with hemicellulose and lignin, which influences their suitability as a reliable source of sugar (Halder *et al.* 2019). The complex structure of lignocellulosic materials' matrix makes them resistant to hydrolysis, and they are particularly resistant to enzymatic hydrolysis (Mkhize *at al.* 2016). The hydrolysis of carbohydrates is a common method of breaking the long sugar polymer chains of cellulose and hemicellulose into their monomeric sugars. These sugars are used in bioenergy, biomaterials, and as chemical precursors. Typically, the hydrolysis process is carried out after the pretreatment step has been completed (Ethaib *et al.* 2018). Maximizing the monomeric sugar *via* the hydrolysis of lignocellulosic materials is among the most challenging subjects in (bio) reactor engineering science at present (Sarip *et al*. 2016). Therefore, an efficient pretreatment process is required to optimize sugar productivity from the sequential hydrolysis process and minimize sugar loss (Ethaib *et al*. 2016a). However, the challenge in the hydrolysis stage is to produce a high sugar alcohol yield from lignocellulosic biomass with reduced chemical and energy use in the pretreatment process to decrease investment costs. In recent decades, a wide variety of physical, chemical, and biological pretreatment approaches have been developed and employed in combination to pretreat lignocellulosic biomass. They aim to modify and disrupt the lignocellulosic matrix *via* the decrystallization of cellulose and removal of lignin/hemicellulose (Abo *et al*. 2019). Each pretreatment method has distinct advantages and disadvantages. Currently, some of these technologies involve severe reaction conditions, relatively low sugar yields, and high processing costs (Zabed *et al.* 2017). Further, some of them require an extra neutralization cycle, as certain chemicals that are released during pretreatment inhibit enzyme activity during hydrolysis and fermentation (Kim 2018). Therefore, the use of a green and low-energy pretreatment is crucial to enhance the enzyme susceptibility of lignocellolusic materials, avoid unnecessary waste, and maximize the efficiency of the end product.

Even though the various categories of pretreatment processes have been individually addressed in several published works, the need for a comprehensive review covering different types of pretreatment processes along with their advantages and disadvantages is beneficial in selecting proper pretreatment process and mitigating the process operational defects besides minimizing the product yield. This review discusses the existing and promising pretreatment approaches for the utilization of lignocellulosic biomass and details their strengths and potential challenges with regard to viability and sustainability.

Importance of Pretreatment

Generally, lignocellulosic biomass includes three main components, which are cellulose, hemicellulose, and lignin. However, it has other minor components, such as ash, pectin, protein, and extractives (Woiciechowski *et al.* 2020). Polymeric sugars are the main components of cellulose and hemicellulose that have the potential to release the monomers (fermentable sugars) during the hydrolysis stage. Monomeric sugars, such as glucose and xylose, can be used for manufacturing other products, such as bioethanol and other sugar alcohol products (Ethaib *et al.* 2020a). Enzymatic hydrolysis is an environmentally friendly technique that uses milder processing conditions than chemical hydrolysis. Acid or alkaline

hydrolysis processes can lead to the formation of sugar by-products that inhibit fermentation microorganisms, such that further detoxification processes are needed (de Araujo Guilherme *et al.* 2019). Improving the sugar yield of enzymatic hydrolysis requires a pretreatment step to break down the recalcitrant aspects of the lignocellulosic biomass (Sharma *et al.* 2019). Hemicellulose fibers serve as glue that fills the voids between cellulose fibers and hemicellulose fibers and wrap around them. The carbohydrate-rich cellulose and hemicellulose are externally coated with lignin, which prevents the degradation of plant cells and serves as a defensive sheath against hydrolyzing enzymes (Sahay 2020). The pretreatment process is done to partially change the matrix structure of lignocellulose by removing lignin and breaking down the structure of cellulose and hemicellulose. Breaking down and modifying the structure of lignocellulosic biomass can enhance enzyme accessibility and facilitate the release of fermentable sugars during enzymatic hydrolysis (Houfani *et al.* 2020). There are several typical units of operation for refining the products required to convert lignocellulosic biomass. The first unit of operation is pretreatment, which is followed by hydrolysis, fermentation, and product recovery (Fig. 1). Several choices exist for each unit of operation, each of which has advantages and disadvantages.

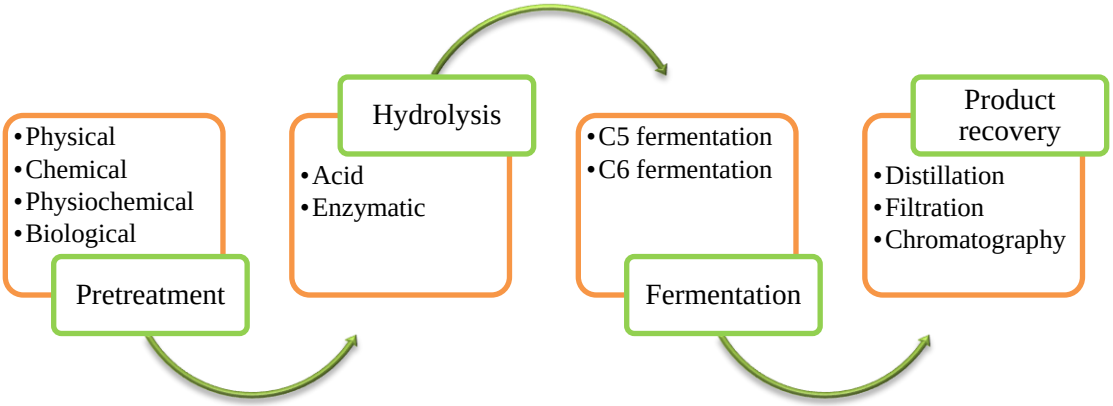

Fig. 1. Typical units of operation of the lignocellulosic conversion process

Therefore, the pretreatment process has a crucial role that must be considered for the successful deployment and production of bio-alcohol compounds from lignocellulosic materials. However, pretreatment can be cost-prohibitive (Antunes *et al.* 2019). Effective and economical pretreatment is essential for successful hydrolysis output and downstream operations (Jørgensen *et al.* 2007). The pretreatment aims to improve access to polysaccharides within lignocellulose and increase susceptibility to hydrolysis (Fig. 2) (Ethaib *et al.* 2015). Pretreatments aim to change the relative content of lignocellulose composition by removing lignin and modifying the hemicellulose and cellulose structure to increase the monosaccharide yield following enzymatic hydrolysis. With appropriate pretreatment, actual sugar yields can reach ≥ 90% of theoretical sugar yields (Zhang and Lynd 2004). Non-pretreated matter has an actual sugar yield of less than 20% of theoretical enzymatic hydrolysis yields. When pretreatment is used, a variety of value-added products can be obtained, which offers several advantages, such as net energy gain, reduced cost, and decreased environmental impact (Batista Meneses *et al.* 2020). There are several essential aspects that should be considered for efficient pretreatment (Jorgensen *et al.* 2007; Alvira *et al.* 2010; Ethaib *et al.* 2016b), which include economic feasibility, energy

consumption, fermentable sugar release, and applicability to a wide variety of feedstocks. In addition, pretreatments can minimise monosaccharide degradation and the presence inhibitory compounds and avoid the use of toxic chemicals during fermentation.

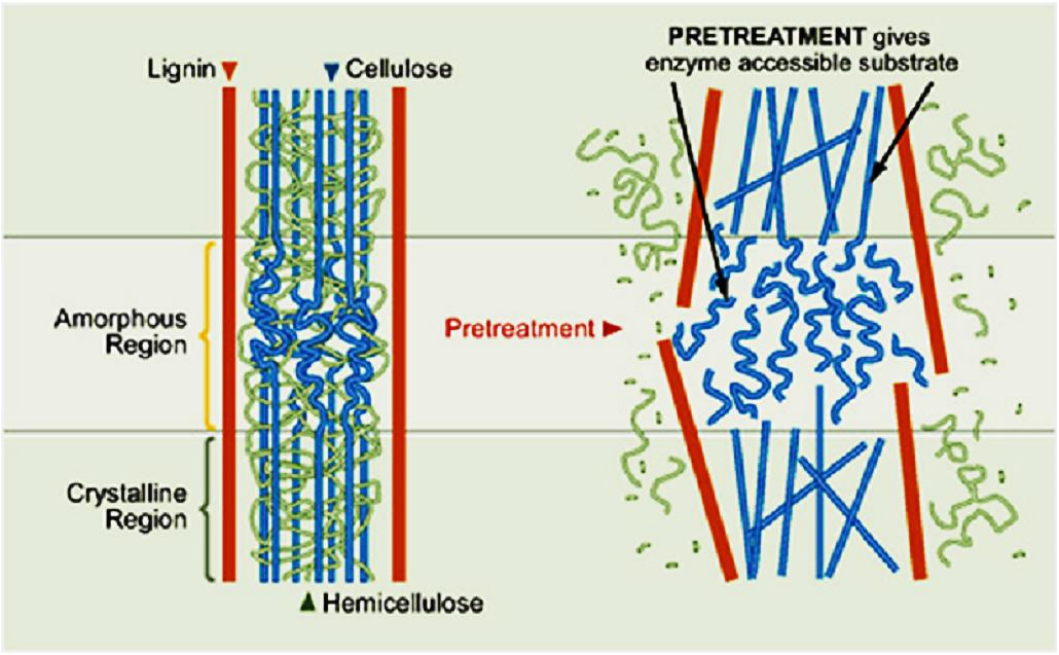

Fig. 2. Schematic of the general effect of pretreatment on the structure of lignocellulosic biomass (adapted from Singh and Satapathy 2018)

Lignocellulosic Biomass

Lignocellulosic biomass is a solid biopolymer that is abundant in nature as dry plant matter and as a low-value by-product from various industries.

Table 1. Potential Sources of Lignocellulosic Biomass Generation

Source	Example	Reference
Municipal solid waste	Kitchen waste, waste paper and cardboard, wood items, and garden residue	Karimi and Karimi 2018; Wang *et al*. 2013; Bai *et al.* 2020
Argo-industrial residue	Empty palm fruit bunches, sugarcane bagasse, sweet sorghum bagasse and sago effluent, and residue from the wood industry	Derman *et al.* 2018; Michelin *et al*. 2016; Boboescu *et al.* 2019; Ethaib et al. 2018
Agricultural residue	Corn stover, palm oil trunk, rice, and wheat straws	da Silva *et al.* 2020; Zhang *et al*. 2018; Yang *et al*. 2017
Cellulosic waste	Paper sludge and pulp	Salameh *et al.* 2020; Alkasrawi *et al. 2020*
Forestry residues	Softwood stems and hardwoods stems	Zhou *et al.* 2015; Normark *et al.* 2014
Energy crops	Switchgrass , Miscanthus, Canola	Bonfiglio *et al*. 2019; Batista Meneses *et al*. 2020 Martins *et al.* 2020

The accumulation of this solid waste results in several environmental issues, safety hazards, and health issues. Furthermore, sustainable cycles can only be attained if a greater proportion of these wastes can be recycled or reused (Erabee and Ethaib 2018; Ethaib *et al*. 2018; Ethaib 2019). Solid waste management practices play a vital role in the promotion of greater resource recovery and sustainable development, which is achieved by recycling, reusing, and energy recovery. As lignocellulosic biomass is biodegradable and represents a large source of renewable organic matter, it is a promising raw material for the production of biofuels and other chemicals due to its remarkable sugar content. Table 1 shows several lignocellulosic biomass sources that can be used in the second generation of bioethanol production.

Table 2. Cellulose, Hemicellulose, and Lignin Content of several Common Lignocellulosic Biomass Sources

Lignocellulosic Biomass Source	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Municipal Solid Waste				
Paper mill sludge, Waste papers from chemical pulps,	28 to 70	10 to 20	5 to 10	Tawalbeh *et al*. 2020; Duncan *et al.* 2020; Sun and Cheng 2002
Waste paper	43-58	7-11	1	Nishimura *et al.* 2016
Energy Crops				
Switchgrass	35 to 39	29 to 35	18 to 32	Yan *et al.* 2010; Kumar *et al.* 2011; Sundar *et al.* 2014
Miscanthus	44 to 45	25 to 30	21 to 26	Batista Meneses *et al.* 2020; El Hage *et al.* 2010
Softwood Stems				
Pine	42	22	30	Normark *et al*. 2014
Spruce	44	21	29	Normark *et al.* 2014
Hardwoods Stems				
Poplar	39 to 47	17 to 19	20 to 25	Wang *et al.* 2012; Zhou *et al.* 2015
Oak	45	25	24	Shafiei *et al.* 2010
Eucalyptus	45	20	28	Romaní *et al.* 2014
Argo-industrial Residue				
Sugarcane bagasse	34 to 38	29 to 31	19 to 25	Michelin *et al.* 2016; Batista Meneses *et al*. 2020
Sago palm bark	41	22	26	Ethaib *et al.* 2020a
Agriculture Residues				
Corn cobs	32 to 35	39 to 41	6 to 9	Sewsynker-Sukai *et al.* 2017; Han *et al.* 2018
Wheat straw	33 to 40	22 to 25	16 to 20	Yang *et al.* 2012; Amiri *et al*. 2014; Michelin and Teixeira 2016
Rice straw	37 to 57	8 to 22	16 to 33	Yang *et al.*2012; Amiri *et al.* 2014; Yang *et al.* 2019

Understanding lignocellulosic materials' chemistry and its polymeric architecture is essential to effectively use biomass to produce high quality and useful end products, such as biofuels and valuable chemicals. The plant cell wall is composed mostly of the plant's dry weight and is comprised of various percentages of cellulose, hemicellulose (both of which are carbohydrate polymers), and lignin (an aromatic polymer), which are closely related in a complicated structure. The contents of cellulose, hemicellulose, and lignin in some common agricultural residues were reported as listed in Table 2.

Cellulose is the skeleton of this structure. The cellulose chains are wrapped in a cross-linked matrix of hemicellulose and enclosed in a protective sheath of lignin. The crosslinking between polysaccharides (cellulose and hemicellulose) and the lignin *via* ester and ether linkages contributes to the recalcitrant nature of the lignocellulosic biomass, which results in reduced access to the polysaccharide molecules by hydrolytic enzymes (Zeng *et al*. 2017) (Fig. 3).

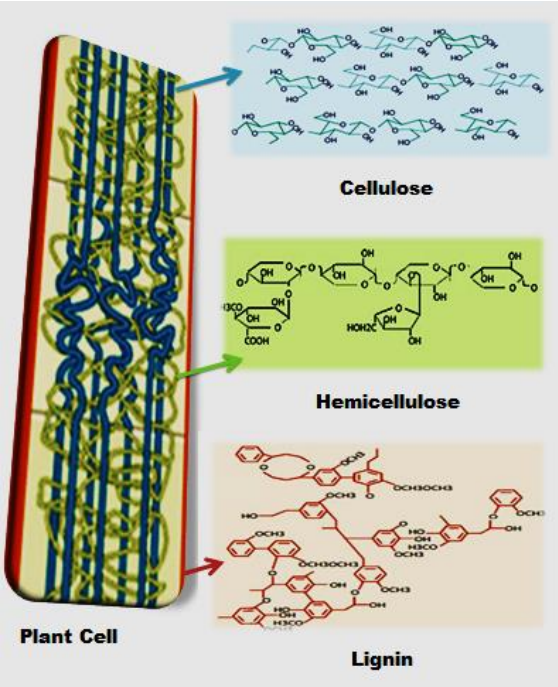

Fig. 3. Plant cell structure

Cellulose is the primary structural constituent in walls of plant cells, and it is responsible for the stiffness and organized fibrous structure. To utilize cellulose in the production of bioethanol and other chemicals, the fermentable D-glucose can be liberated from cellulose *via* either chemical or biological means by cellulolytic enzymes that break the β-1-4 glycosidic linkages; the liberated glucose can then be subjected to the fermentative microorganisms (Robak and Balcerek 2018). Unlike cellulose, which has the same structure in all lignocellulosic biomass, hemicellulose is a heteropolymer that varies in structure and composition and can be classified according to these variations (Wayman *et al.* 2005). Hemicelluloses are classified into four groups according to the main kind of sugar residue present in them: xyloglucans, xylans, mannans, and mixed-linkage β-glucans. Xylan hemicellulose is the most prevalent hemicellulose class in hardwoods, grasses, and straws, and minor amounts of galactomannans are also present. In contrast, glucomannans and galactomannans constitute the majority of mannan-type hemicelluloses,

which are the predominant hemicelluloses in the secondary cell walls of conifers and softwoods (Schädel *et al.* 2010). All hemicellulose polymers are composed of five-carbon sugars (C5) (*e.g.*, xylose and arabinose) and/or six-carbon sugars (C6) (galactose, mannose, glucose, and 4-O-methyl-D-glucuronic acid) (Marais 2009). Lignin is a rigid material that plays a crucial role in tightening cell plant structures by binding cellulose and hemicellulose together. It is a complex aromatic polymer that consists of three basic phenylpropane units, which include p-coumaryl alcohol, coniferyl alcohol, and synapyl alcohol (Cesarino *et al*. 2012). The complex structure of lignin (the presence of numerous kinds of carbon-carbon and ether bonds between individual monolignols) causes the formation of dimers, trimers, and tetramers that then form random links with each other. Robust carbon-carbon bonds are mainly responsible for the barrier-type nature of lignin (Keshwani 2009).

Pretreatment Methods

Many studies have investigated different pretreatment approaches, and they have followed various procedures to evaluate pretreatment efficiency.

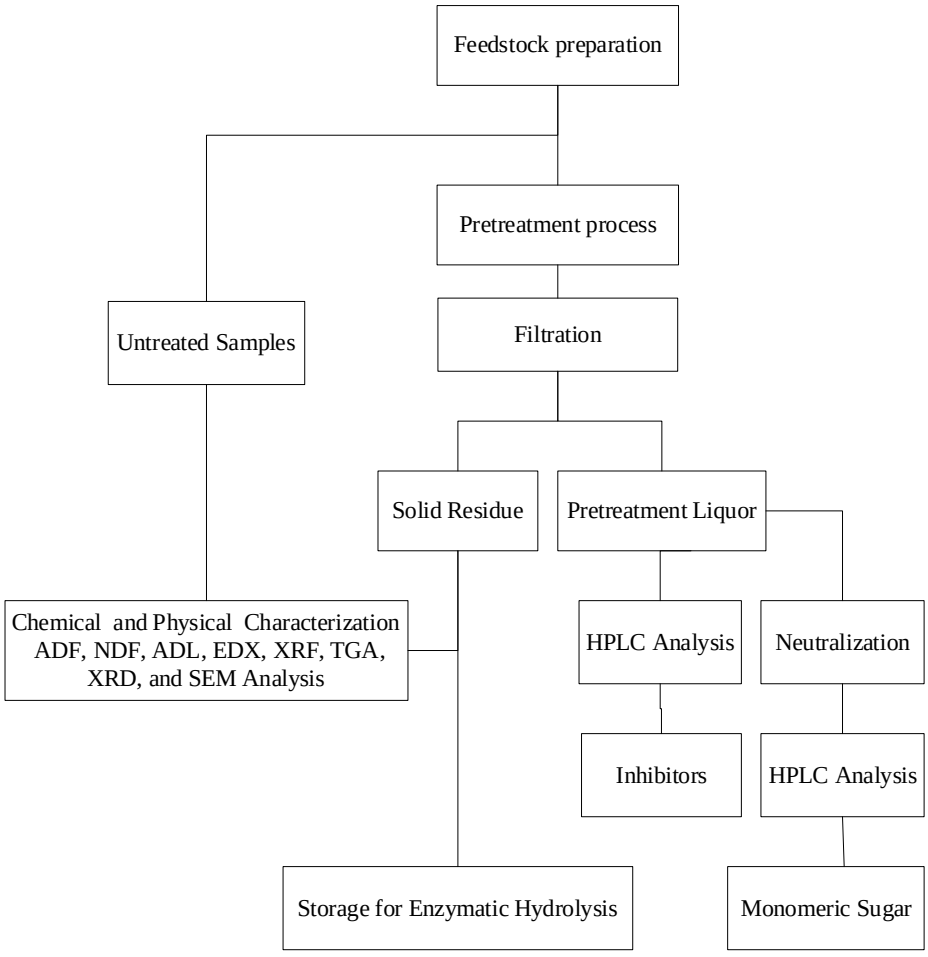

Fig. 4. Pretreatment process-flow diagram: High-performance liquid chromatography (HPLC); neutral detergent fiber (NDF) analysis; acid detergent fiber (ADF) analysis; acid detergent lignin (ADL) analysis; energy dispersive X-ray (EDX); X-ray fluorescence (XRF); thermogravimetric analysis; X-ray diffraction (XRD); scanning electron microscopy (SEM)

As a suggestion for lab study, the following flow chart (Fig. 4) can be considered to identify the effectiveness of the pretreatment method. Pretreatment methods can be divided into different groups, which include physical methods (*e.g.*, milling and grinding), chemical methods (*e.g.*, dilute acid, alkali, organic solvents, and oxidizing agents), physical-chemical methods (*e.g.*, steam explosion, carbon dioxide explosion, and microwave-assisted pretreatment), biological methods, or a combination of the above approaches, which are discussed in the following subsections.

Physical methods

Physical pretreatment can increase the accessible surface area, increase pore size, decrease the crystallinity and degree of polymerization of cellulose, minimize the amount of chemicals used during processing, and reduce post-treatment processing of chemical wastes (Moset *et al.* 2018). For physical pretreatment, most studies have employed mechanical methods, such as gridding and chipping, to reduce the particle sizes of biomass feedstocks. Different types of physical processes can be applied as a pretreatment, such as milling, ball milling, two-roll milling, hammer milling, colloid milling, and vibro-energy milling. Irradiation technologies, such as gamma rays, electron beams, microwaves, and ultrasounds, are also applied to improve the enzymatic hydrolysis or biodegradability of lignocellulosic waste materials (Pérez-Rodríguez *et al.* 2017; El Achkar *et al.* 2018; Gu *et al.* 2018; Zhang *et al.* 2018). In general, physical methods contribute to high processing costs due to high energy consumption. In addition, the physical methods remove less lignin from the cell wall structure than chemical pretreatment. Therefore, physical processes are often combined with another kind of pretreatment (*e.g.*, chemical pretreatment) to improve performance.

Chemical methods

Historically, chemical pretreatment is the oldest method used for cellulose saccharification. Various chemical agents have been employed in chemical pretreatments, such as acids, alkalis, ozone, organic solvents, and peroxide. Concentrated acids, such as H_2SO_4 and HCl, have also been applied in the pretreatment process and can result in improved release of fermentable sugars *via* enzymatic hydrolysis. Chemical pretreatment has been widely applied for a wide range of biomass feedstocks and has proven its efficiency due to the ability of the acidic environment to remove hemicellulose and solubilize lignin to enhance cellulose hydrolysis. However, these powerful agents are toxic and corrosive, so they require special reactors that increase cost (Peral 2016). Diluted acids are the preferred option for lignocellulose pretreatment due to their capacity to achieve high reaction rates and enhance the subsequent process of biomass hydrolysis. Additionally, diluted acids reduce the negative effects of using concentrated acids, such as equipment erosion and the formation of inhibitor compounds (Bhutto *et al.* 2017). Dilute-acid pretreatment is typically performed at low temperatures ($T < 160$ °C) for batch processing and high temperatures ($T > 160$ °C) for continuous-flow processing (Cheng 2017). Dilute sulfuric acid is the most commonly used acid for the pretreatment of various biomass feedstocks. Among acidic solutions, H_2SO_4 is the preferred option for acidic pretreatment (Santos *et al.* 2018; Shimizu *et al.* 2018; Xavier *et al.* 2018). Despite the efficiency of diluted acid, there remains a concern about the formation of inhibitors (Jędrzejczyk *et al.* 2019), such as hydroxymethylofurfural (HMF), furfural, and acetic acid. In addition, a pH-neutralization process of pretreatment liquor for further enzymatic hydrolysis process is required.

For alkaline pretreatment, the process is performed by adding diluted bases, such as sodium, calcium, and potassium hydroxides or anhydrous ammonia, to biomass mixtures to break down the links between the lignin and other polymers. The reactions improve the delignification process *via* disrupting the lignin structure and removing the lignin that decreases the mechanical strength of the plant cell. Consequently, enzymes have increased access to the cellulosic compounds inside the cell, and the release of sugar from treated material during hydrolysis is improved (Ethaib *et al*. 2020b). The alkaline pretreatment can be performed at room temperature by soaking the biomass or at elevated temperatures (Sivanarutselvi *et al.* 2019). The key benefits of alkaline pretreatment are the affordability of the chemicals, the mild reaction conditions, the high removal of lignin, and the possibility of biomass fractionation. Hydrogen peroxide has been applied to reduce the lignin content in lignocellulosic biomass (Ho *et al.* 2019). In this technique, the substrate is saturated in pH-adjusted water (*e.g.*, to pH 11 to 12 using NaOH) that contains H_2O_2 at room temperature for approximately 6 h to 24 h. This process can enhance enzymatic hydrolysis outcomes as a result of the delignification process. Song *et al.* (2016) documented that, after alkaline peroxide pretreatment, bamboo substrates can be converted into useful sugars with a sizable yield *via* enzymatic hydrolysis. In another study, Saha and Cotta (2007) found that performing dilute alkaline peroxide pretreatment using 7.5 wt% H_2O_2 at 35 °C for 24 h can also result in an excellent conversion (96%) of rice hulls into fermentable sugars after enzymatic saccharification. Measurable furfural and HMF were determined in the process, making it more fermentable/digestible compared to a dilute-acid pretreatment. The main drawback of the initial alkali treatment is the long processing time and difficulties with the neutralization of the post treatment mixture (Bhutto *et al.* 2017). Therefore, many have attempted to combine both acid and alkali pretreatments to enhance the subsequent hydrolysis yield (Weerasai *et al.* 2014). Acid pretreatment enhances hemicellulose removal as a first stage. Then, alkali pretreatment is employed for more lignin removal as a second stage, which eventually results in pure cellulose.

Ozone has been applied successfully for the pretreatment of lignocellulosic materials, and it effectively degrades lignin and some hemicellulose; the process is known as 'ozonolysis' (Ab Rasid *et al.* 2020). This pretreatment is typically implemented at low temperatures to decrease the formation of inhibitory compounds (Ballesteros *et al.* 2018). However, because a large amount of ozone is needed for ozonolysis, it can be an expensive process (Sun and Cheng 2002).

Organosolv pretreatment can also be utilized to facilitate the hydrolysis of lignocelluloses. An (aqueous) organic solvent acts a delignification agent (Nitsos *et al.* 2018). During the organosolv pretreatment, the lignocellulosic materials are combined with organic liquid and water. Then they are heated to remove lignin, hydrolyze some of the hemicellulose, and leave reactive cellulose in the solid phase (Choi *et al.* 2019). A wide array of organic or aqueous organic solvents at temperatures of 140 °C to 200 °C can be utilized with or without the addition of catalysts, such as acetylsalicylic, salicylic, and oxalic acids. A variety of organic solvents such as alcohols, esters, ketones, glycols, organic acids, phenols, and others have also been successfully applied (Zhang *et al.* 2016). However, some aspects should be considered to decrease the operational costs of the process such as the price of solvents and the simplicity of solvent recovery. For instance, the applied solvents should be recovered by evaporation and condensation and then recycled and reused in the subsequent pretreatment batches. Moreover, the removal of solvents from pretreated biomass is an essential step because they may inhibit enzyme hydrolysis and the fermentation or digestion of hydrolysate (Sun and Cheng 2002).

More recently, ionic liquids, such as 1-ethyl-3-methylimidazolium acetate 1-allyl-3-methylimidazolium chlorides, have been applied in the pretreatment process to dissolve lignocellulosic material components and improve enzymatic hydrolysis. Depending on the selection of anions and cations, ionic liquids have tunable properties (Yoo *et al.* 2019). These chemicals are salts generally formed by large organic cations and small inorganic anions. Typically, ionic liquids are considered as green solvents, and they frequently display low vapor pressure, wide liquids range, and efficient dissolution power (Mäki-Arvela *et al.* 2010). Recent research has shown that various ionic liquids (*e.g.*, [EMIM][CH_3COO] and [EMIM][CH_3COO]) are capable of dissolving cellulose and lignin, and they are easily regenerated from these solutions (Reddy 2015). However, to prevent the depolymerisation of cellulose and the formation of low molecular products, the optimum dissolution conditions should be determined (Mäki-Arvela *et al.* 2010).

Physical–chemical methods

Processes that combine both physical tools and chemical agents to perform pretreatment processes are referred to as physicochemical processes. These processes can be considerably more effective than physical processes alone. Steam explosion is the most researched method of physicochemical processes. In steam explosion, the pressure is suddenly reduced, which makes the materials undergo an explosive decompression (Auxenfans *et al.* 2017). The elevated pressure and consequent high temperature in a short period (pressure ranges from 7 to 4.8 MPa and temperature ranges from 160 °C to and 260°C) for a few seconds (*e.g.*, 30 s) to several minutes (*e.g.*, 20 min) have been used in this approach (Agbor *et al.* 2011; Pielhop *et al.* 2016; Baêta *et al.* 2017; Bonfiglio *et al.* 2019). Due to the several advantages shown by this treatment, such as short time, lack of chemicals usage, and low energy consumption, this process can be economically affordable. However, there are other concerns about the poor lignin removal, deconstruction of xylan into hemicellulose, and possibility of generating inhibitory chemicals during processing at high temperatures (Bhutto *et al.* 2017). Thus, steam explosion pretreatment can be performed with the addition of different chemicals, such as organosolvents and sulphuric acid to promote hemicellulose hydrolysis, enhance lignin solubilisation, and decrease the formation of inhibitors if lower temperatures are applied, and thereby improve enzyme accessibility to cellulose in further processing (Guerrero *et al.* 2017; Martino *et al.* 2017).

Ammonia fibre/freeze explosion (AFEX) is a physico-chemical pretreatment process (Mathew *et al.* 2016). Similarly to steam explosion pretreatment, during the AFEX the biomass is exposed to pressure around 0.7 to 2.7 MPa and liquid ammonia at relatively high temperatures (*e.g.*, 90 to 100 °C) for 30 min followed by an immediate reduction in pressure. The effective factors in the AFEX process are ammonia loading, temperature, water loading, blowdown pressure, time, and number of treatments (Chundawat *et al.* 2020). The ammonia can lead to degradation of hemicellulose to oligosaccharides and alter the lignin structure and swell of the biomass cell plant, which cause an increase in the available surface area for enzyme accessibility (Jędrzejczyk *et al.* 2019). Nevertheless, AFEX has low efficiency when pretreating biomass with high lignin content and requires a large amount of ammonium, which requires high energy input for recovery and recycling (Rabemanolontsoa and Saka 2016).

Carbon dioxide explosion is another pretreatment technique based on the concept of a supercritical CO_2 explosion (Al Afif *et al.* 2020). This procedure is achieved at a lower temperature than steam explosion. Supercritical fluid refers to a fluid that is in a gaseous

form but is compressed at temperatures above its critical point to a liquid-like density. It is hypothesized that because CO_2 forms carbonic acid when dissolved in water, this acid increases the hydrolysis rate. The enzymatic digestibility of various biomass feedstocks, such as green coconut fiber (Putrino *et al.* 2020) and soy sauce residue, have been reported (Xiang *et al.* 2019). In addition, it was documented that low levels of the fermentation inhibitory compounds of hydroxymethylfurfural, furfural, and acetic acid was detected during pretreatment guayule biomass by supercritical CO_2 in the presence of water (Islam *et al.* 2018). The key benefits of the supercritical CO_2 method are the short amount of time required and increased sugar yield. However, the supercritical CO_2 process might be too expensive for industrial application, thus further optimization is needed (Carneiro *et al.* 2016).

Liquid hot water (LHW) is one of the historical hydrothermal pretreatment approaches used in the pretreatment of lignocellulosic materials for bioethanol production (Ximenes *et al.* 2017). In this procedure, the pressure is used to maintain water in a liquid state at an elevated temperature. To maintain water in the liquid state, the pressures for this process are usually > 5 MPa at temperatures ranging between 160 °C to 230 °C (Kim *et al.* 2014; Ko *et al.* 2015). Water under high pressure can penetrate into the biomass, hydrate cellulose, and remove the hemicellulose and some lignin. Approximately 40% to 60% of the total biomass is dissolved using this process, and 4% to 22% of the cellulose, 35% to 60% of the lignin, and all of the hemicellulose removed (Kumar *et al.* 2009). In liquid hot water pretreatment, no chemicals are added, and the pretreatment conditions are kept simple, utilizing just water, heat, and pressure to alter the biomass material. Liquid hot water pretreatment allows enzyme inhibitors to be released and can expose and modify lignin that adsorbs proteins of enzymes, which in turn interferes with the delivery of enzyme activity to the cellulose substrate (Ximenes *et al.* 2017).

Recently, microwave-assisted pretreatment is a technology that has brought wide attention to the biomass conversion industry. This technology utilizes both thermal and non-thermal effects of microwave energy (Ethaib *et al.* 2020). Microwave-assisted pretreatment can be synergistic with chemicals, such as acid, alkaline, and organic solvents, to enhance the yield of the follow-up enzymatic hydrolysis (Ethaib *et al.* 2017; Zhang *et al.* 2020). A pretreatment process based on microwave heating can achieve a green and low-energy process. The minimal use of energy requirements and chemical auxiliaries, such as microwave heating for a short time and the extremely diluted solvents, meet with the principles of green-extraction. However, microwave heating technology has not completely replaced conventional industrial heating systems. Many microwave-assisted application studies have been conducted. The challenges associated with processing different biomass wastes materials using microwaves are related to the inherent problems with the microwaves themselves and the raw material characteristics. For instance, not all materials (*e.g.*, transparent material) are easily heated *via* microwave heating. Accordingly, the efficacy of microwave-assisted pretreatment relies ultimately on the operating conditions. The most influential factors on sugar recovery during microwave-assisted pretreatments are exposure time, microwave power, solvent type, and solid loading (solvent to feed ratio) (Ma *et al.* 2009; Ethaib *et al.* 2018, 2020c).

Over the years, performing the pretreatment process with the assistance of ultrasound irradiation has gained increasing interest. It was reported as a good way to induce structural changes in the lignocellulosic biomass to enhance enzymatic saccharification (Wang *et al.* 2017). Ramadoss and Muthukumar (2014) recorded that ultrasound-assisted ammonia pretreatment of sugarcane bagasse led to a cellulose recovery

efficiency of 95.8% and a 58.1% lignin removal efficiency. Similarly, pretreatment that combined ultrasound and potassium permanganate to pretreat spent coffee waste resulted in 98% cellulose recovery and 46% delignification (Ravindran *et al.* 2017). Further, two ultrasound-assisted pretreatment procedures, which include ultrasound-assisted ionic liquid tetrabutylammonium hydroxide ([TBA][OH]) and ultrasound-assisted alkaline, are successfully conducted to enhance enzymatic saccharification of Eucalyptus (Wang *et al.* 2018a). Several of the challenges facing the ultrasound as a pretreatment technique include the factors related to energy efficiency and the costs of the technique. This seriously challenges the energy efficient quality of the pretreatment technology and may reduce the cost-effectiveness of scaling-up the technology (Bussemaker and Zhang 2013).

Mechanical activation *via* intense milling accompanied by metal salts can be applied for the pretreatment of cellulosic materials to improve enzymatic digestibility. This combined technology utilizes the synergistic interaction of mechanical activation and metal salt in the solid-phase condition (Zhang *et al.* 2015). The intense milling can lead to size reduction and structural disorder of the lignocellulosic biomass and cause the distorting and rupture of chemical bonds. Metals salts are especially fascinating as pretreatment agents due to their lower corrosiveness than inorganic acids (Xu *et al.* 2018). The common metal salts, such as the chlorides, nitrates, and sulfates of Al, Fe, Mg, and K, are typically selected for this pretreatment (Sewsynker-Sukai and Guegim Kana 2017; Wang *et al.* 2018b). Typically, the metal salt pretreatment is carried out in the molten state or in an aqueous solution due to the poor contact between metal salts and cellulosic materials in the solid-phase condition (Loow *et al.* 2015). Thus, the mechanical activation *via* the intense milling facilitates metal salt movement and contact with lignocellulosic materials in the solid phase. Furthermore, there is a possibility to recycle and reuse the metal salts in the biomass pretreatment. Recovery of the metal salts can be carried out *via* ultrafiltration in the form of metal hydroxides and treatment with conjugated acids to convert these hydroxides back to metal chlorides. However, some prospects and challenges exist with the use of inorganic salts. For instance, Zhang *et al.* (2019) reported that combination of a stirring ball mill with $AlCl_3$, $FeCl_3$, Al $(NO_3)_3$, and $Fe(NO_3)_3$ for pretreatment improved the enzymatic saccharification yield of sugarcane by bagasse 79.7%, 65.4%, 65.2%, and 69.0%, respectively. In contrast, a huge fluctuation of enzymatic hydrolysis yield was reported by Liu *et al.* (2009) and López-Linares *et al.* (2013), which ranged from 36.6 to 98.0%. This might be related to the inhibitory effects of metal ions that remain in the solid fraction, which might cause undesirable impacts on enzymes during the bioconversion stage (Tejirian and Xu 2010). It was reported that the heavy metal elements, such as chromium could cause inactivation or a denaturing of cellulase enzyme. Beyond the low understanding of the influence of various inorganic salts on cellulase hydrolysis, there is a concern about the economic feasibility of this type of pretreatment due to the extreme energy consumption required by these processes (Loow *et al.* 2015).

Biological methods

Biological pretreatment can be applied using microorgansims to treat biomass and enhance enzymatic hydrolysis or the fermentation rate. The use of microoragansims includes many bacteria strains, such as *Actinomycetes*, *Bacillus*, *Candida*, *Streptomyces*, and some known fungi species, such as *Aspergillus*, *Ceriporia lancerata*, and *Cyathus stercolerus*, exhibit the ability to degrade lignocellulosic biomass (Pandey *et al.* 2014; Poszytek *et al.* 2016; Nikiema *et al*. 2017). Earlier published articles reported that an effective delignification process of various lignocellulosic biomasses was carried out using

various types of microbes that enhance the digestibility of organic matter (Maurya *et al.* 2015; Madadi and Abbas 2017). Biological pretreatments have low energy requirements and are carried out under mild environmental conditions. However, almost of these procedures are very slow and require long incubation times, which limits their application at an industrial level (Zabed *et al.* 2019).

Table 3 summarizes some of the advantages and disadvantages of the pretreatment methods that have been examined to date.

Table 3. An Overview of Some Features of Various Pretreatment Technolgies

Pretreat-ment	Process Type	Advantages	Disadvantages
Physical	Ball milling; Hammer milling	Intensive decrysallization of cellulose and particle size reduction	High energy requirements
Chemical	Acid	Alters lignin structure and faciltates the hydrolysis of hemicellulose into xylose and other sugars	Formation of toxic substances, high cost, and equipment corrosion
	Alkaline	High lignin removal and biomass swelling causes an increase in the accessible surface area for enzymes	Irrecoverable salts formed and incorporated into biomass and long retention time is required
	Organosolvent	Hydrolyzes lignin and hemicelluloses	High reagent costs, high capital investment, and formation of inhibitors
	Ozonolysis	Effectively reduces lignin content from cellulosic material without generating inhibitors	Expensive and requires a large amount of ozone
	Ionic liquids	Mild operation conditions for lignin removal	High solvent cost and need for solvent recovery and recycling
Physical-chemical	Steam explosion	Causes high hemicelluloses fractions, hydrolysis, and lignin degradation, and it is cost-effective	Not effective with softwood and forms inhibitory compounds
	Ammonia fiber explosion (AFEX)	Removes lignin and hemicellulose to a certain extent, increases accessible surface area, and forms toxic end-products	Not suitable for high lignin materials and requires recovery steps for ammonia
	CO_2 explosion	Increases accessible surface area and does not cause formation of inhibitory compounds	Does not modify lignin or hemicelluloses and has high cost
	Liquid hot water	The majority of hemicelluloses can be dissolved	High temperature and pressure
	Microwave-assited chemical process.	Can modify lignocelluosic structure in short time	Not effecitive with transparent material, and the pretreatment solvent should be a good absorber with a high dielectric loss
Biological	Fungi and actinomycetes	Environmentally friendly and requires low use of energy and chemicals	Low rate of bioconversion

Techno-Economic Overview on Pretreatment Technologies for Bioethanol Production

Pretreatment technologies must sustain the high product yields in the subsequent processes such as enzymatic hydrolysis and fermentation with minimal conditioning costs and lower loss of sugars during conditioning (Wyman *et al.* 2005). In this context, many economic aspects affect the end product visibility and process economics. The ultimate purpose for developing such a detailed process design, simulation model, and cost estimate is to determine the economics of chemical or biofuels production (Davis *et al.* 2018). The total capital investment cost, the operating cost, and the net present value of the investment, *etc.* should be considered in the cost analysis for any pretreatment process economics for the conversion of lignocellulosic biomass to hydrocarbon fuels and co-products. In order to understand the effect of a pretreatment lowered price on the economics of ethanol production, some studies report the minimum ethanol selling price (MESP) in the techno economic analysis: "the MESP is the price of the biofuel that would make the net present value of the ethanol facility equal to zero over its 25-year lifetime" (George *et al.* 2015). However, many factor have direct effect on the MESP such as the price of feedstock, the transportation cost, the feedstock chemical composition, the pretreatment efficiency for the cellulose conversion to glucose, enzyme cost and its loading, fermentation effectiveness, the ethanol yield, the size of plant facility, investment costs, energy cost, and cost recovery system (Tao *et al.* 2011).

Regardless the other factors that have influenced the MSEP, a limited number of studies have reported the pretreatment cost impact on the industrial scale lignocellulosic bioethanol productions processes based on pretreatment process synthesis, simulation and evaluation. Tao and his team examined 6 types of pretreatment processes including AFEX, dilute acid, lime, LHW, soaking in aqueous ammonia (SAA), and sulfur dioxide-impregnated steam explosion (SO). They found that feedstock cost (switchgrass) contributed by 45 to 53% of the MESP for the six cases. The resulting MESPs were $2.74/gal for AFEX pretreatment (with closely comparable MESPs for diluted acid and SO pretreatment), $3.3/gal for LHW pretreatment, and $4.07/gal for SAA pretreatment. An earlier study carried out by Eggeman and Elander (2005), 5 types of pretreatment processes for the liberation of sugars from corn stover. They constructed ASPEN Plus (Aspen Technology, Inc., Cambridge, MA) simulation models for dilute acid, hot water, AFEX, ammonia recycle percolation (ARP), and lime pretreatment processes, which were compared on a consistent basis. The MESP across the pretreatment cases were $1.35/gal, $1.35/gal, $1.70/gal, $1.40/gal, and $1.65/gal for dilute acid, hot water, AFEX, ARP, and lime pretreatment processes, respectively. Meanwhile, the MESP was $6.45/gal for the no pretreatment case operation. In another research study, George *et al.* (2015) made a techno-economic modeling for the cost of ionic liquids (IL) pretreatment using a number of ionic liquids in this process. The selected ionic liquids were compared to a benchmark system containing the IL 1- ethyl-3-methylimidazolium acetate [C im][OAc]. They found that the MSEP was > $6/gal due to the high purchasing cost of ILs. Therefore, replacing the non-recovered IL with high recycle IL should be considered as a primary design criterion of IL pretreatment. da Silva *et al*. (2016) simulated different pretreatment scenarios including diluted acid, LHW, and AFEX processes for bioethanol production from corn stover. The pretreatment processes scenarios were performed using different operating conditions such as temperature, pressure, catalyst loading and water content, as well as solids loading. Five scenarios were suggested for each LHW and AFEX and compared with diluted acid pretreatment. They found that the best MSEP value was of $1.78/L for LHW pretreatment

using temperature reactor 190 °C and pressure 13 kPa, and water content 81% and solid loading 23%. Changing the pretreatment conditions led to change MSEP, indicating that the temperature has a great influence on both the ethanol concentration and the total energy consumption, leading to higher MSEP. Similar observations were recorded during the AFEX pretreatment scenarios. The best value of MSEP was $1.80/L, which was achieved by the first scenario of AFEX pretreatment. In this case of pretreatment the corn stover was pretreated under temperature reactor 90 °C, pressure 5 kPa, water content 60%, catalyst loading 1:1, and solid loading 20%. It is important to mention that the MESP of diluted acid pretreatment in this study was $2.55/L. The overall concept suggests that at the production scale for mature bioethanol technology at low costs, the key process parameters of pretreatment should be determined by sufficiently realizing their effects to improve the technology and the production costs.

CONCLUDING REMARKS

Pretreatment techniques were found to be advantageous to facilitate the subsequent unit operations of the lignocellulosic conversion process. Despite the positive impacts of current pretreatment processes on the recovery of valuable soluble components from raw materials, several defects must be addressed. The defects should be remedied to make pretreatment an environmentally friendly, energy-efficient, cost-effective, and simple as possible that is applicable to a wide range of biomass feedstocks. Further, it should ensure the purity of the obtained products. Future research and more efforts are needed to optimize and improve these technologies to decrease energy consumption, effectively utilize auxiliary chemicals, and prevent the formation of inhibitory compounds. Additionally, feasibility research is necessary to assess the viability of each pretreatment type toward commercial-scale pretreatment for bio-energy production using lignocellulosic biomass.

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