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Pretreatment and conversion of lignocellulose biomass into valuable chemicals

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In the past three decades, many studies on the production of biofuels and other chemicals have been conducted using renewable sources such as lignocellulosic biomass. Lignocellulosic biomasses are abundantly available in most countries and furthermore they are carbon neutral. However, the main problem in utilizing lignocellulosic materials lies in the recalcitrance of its bonding. This review provides a comprehensive overview and a brief discussion on producing biofuel and valuable chemicals from lignocellulose biomass. Various aspects of the physical, chemical, thermophysical, thermochemical and biological pretreatment of lignocellulosic materials are discussed in this review. The success in biofuel and chemical production strongly depends on the pretreatment method used. Overall, pretreatment is the major step in the successful production of valuable products from lignocellulosic biomass.

1. Introduction

The depleting of fossil oil resources has become a major reason to develop sustainable sources of renewable energy and chemicals.[1,2] Apart from the scarcity of fossil oil as the main energy resource for transportation and industry, global warming is also considered as one of the major problems that we face today. An Intergovernmental Panel for Climate Change (IPCC) estimated that the contribution of CO_2 to total greenhouse gas (GHG) is approximately 53%.[3,4] In 2009, the European energy and climate package set four targets for 2020 in connection with GHG emissions: 20% reduction of GHG emissions, 20% energy efficiency improvement, 20% share of renewable energy for gross final energy usage, and 10% renewable energy in the transportation sector.[5]

In the past decades, renewable fuels or biofuels were produced mostly from primarily food crops such as cereals, sugar cane and oil seeds (called 1st generation biofuels). Biofuels produced from these primary food crops have considerable economic value; however, their potential to meet transport fuel targets is limited by:[6]

- Competition for land and water used for food and fiber production,
- High production and processing costs that often require government subsidies in order to compete with petroleum products, and
- Widely varying assessments of the net GHG reductions once land-use change is taken into account.

Recently, the 2nd generation biofuels gained interests from many research groups because of the abundantly available feedstock in most countries. Lignocellulosic biomass is a renewable and carbon neutral material that can be converted into biofuel and other intermediate chemicals through various conversion routes.[7] It consists of biopolymer such as cellulose (40–60%), hemicellulose (20–40%), and lignin (10–24%).[8] The most common lignocellulose biomass that has been used as raw materials for chemicals derivative platform are given in Table 1. Lignocellulosic materials also have been widely utilized as intermediate liquid fuel or chemical products such as furfural, levulinic acid, and GVL.[12–14]

Cellulose, a crystalline polymer consists of β-linked chains, has a general formula of $(C_6H_{10}O_5)_n$. Rigidity and strength of a plant's cell wall is conferred by hydrogen bonding between the hydroxyl groups of glucose and the oxygen molecules in cellulose that creates micro fibrils which are connected in a carbohydrate matrix.[15,16] Hemicellulose is a complex amorphous polymer with varying degree of branching and has lower molecular mass than cellulose. It is closely related, both chemically and structurally, to cellulose. However it differs from cellulose by the type and amount of monosaccharides that made up its structure which is generally consisted of xylose (the most abundant), galactose, glucose, arabinose, mannose and sugar acids.[17] It is preferable to remove hemicellulose during pretreatment, because hemicellulose creates a cross-linked network for the structural integrity of cell walls by binding to cellulose micro-fibrils, lignin and pectin.[16,18] After cellulose and hemicellulose, lignin is considered as the most abundant natural polymer on earth.[19] It is the third main constituents of

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Table 1 Lignocellulosic feedstock production,[9] composition[a,10] and prices[b,11]

Feedstock	Global production (2011)	Cellulose	Hemicellulose	Lignin	Price
Wheat straw	1056 million tons	35–39%	22–30%	12–16%	46
Bagasse	501 million tons	25–45%	28–32%	15–25%	40
Corn stover	1413 million tons	35.1–39.5%	20.7–24.6%	11–19.1%	83

[a] In % dry wt. [b] In $/dry ton.

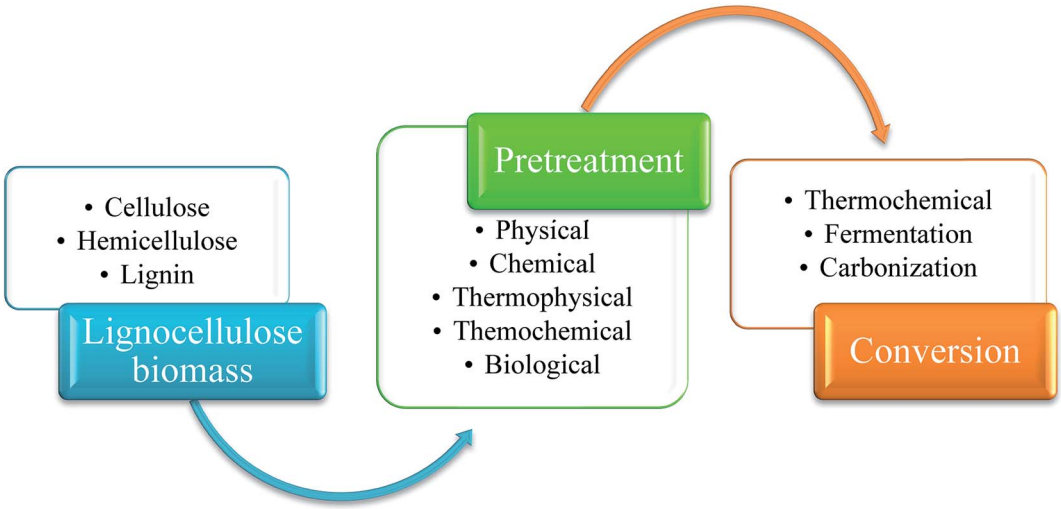

Fig. 1 Schematic diagram showing utilization of lignocellulose biomass.

lignocellulosic biomass, an amorphous polymer matrix from random polymerization of three primary phenylpropane monomers: coumaryl, coniferyl and sinapyl alcohols.[20,21] These three lignin precursors inflict the H (*p*-hydroxyphenyl), G (guaiacyl), and S (syringyl) which can be acylated and show different abundances depend on their origin.[22] Since lignin is always fragmented during extraction and composes of several types of substructures which repeat in haphazard manner, it is difficult to determine the degree of its natural polymerization.[23] These 3 main elements in lignocellulose material present a very complex structure and are organized together with acetyl groups, minerals and phenolic substituents.[24,25] Also the utilization of lignocellulosic biomass depends on its components, because there is difference in reactivity from the interactions into extensive and complex molecular systems between cellulose, hemicellulose and lignin fractions.[25] Thus, pretreatment is needed to break down the complex bonding of these 3 major components in biomass. After pretreatment, the next step is to convert them into desired chemical products. Schematic diagram of the process is shown in Fig. 1.

Utilization of lignocellulosic biomass as raw materials for fuels and other chemicals has already been established in industrial scale, but still there is debate about the pretreatment of this material. To convert this non-edible biomass into valuable products as a sustainable source of energy and chemicals raises many challenges. One of the challenges for biofuel production is how to efficiently reduce high oxygen content from biomass and to produce biofuel with high energy density and with physical and chemical characteristics similar to fossil fuel.[26] Another challenge that still need to be resolved is how to use the waste lignin after pretreatment. Lignin can be used as a feedstock to produce valuable chemicals. The focus of this review is to discuss comprehensively the pretreatment of lignocellulosic biomass, and production of high value chemical products from the pretreated biomass.

2. Pretreatment

Due to its natural recalcitrance, degradation of lignocellulosic biomass is hard. For the utilization of this material as the precursor for bio-fuel and other chemicals production, pretreatment is required to improve material accessibility. The rate of accessibility and digestibility is affected by these main factors:[25,27]

- Crystallinity of cellulose,
- Hemicellulose disruption,
- Accessible surface area (porosity),
- Lignin protection,
- Association of cellulose–hemicellulose–lignin.

Cellulose is considered as the main contributor for the crystalline part, whereas hemicellulose and lignin are amorphous polymer. Lignin acts as a barrier to prevent cellulose and hemicellulose degradation. The removal of lignin will result in hemicellulose removal too, since lignin is chemically connected

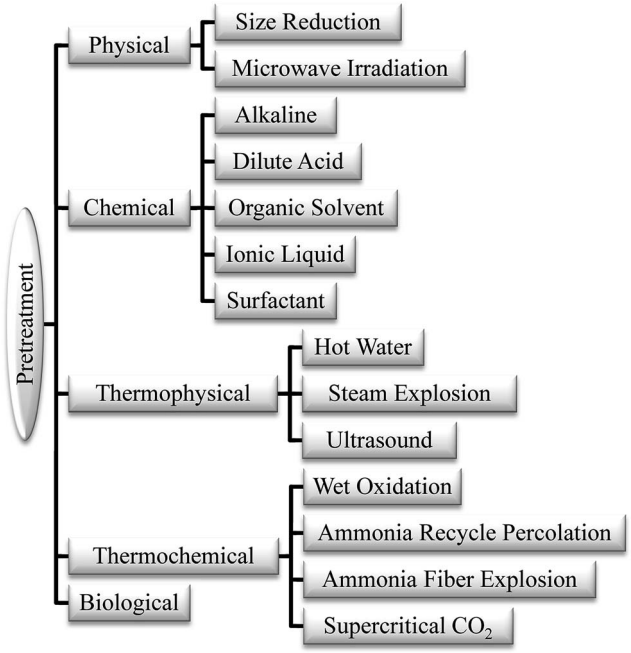

Fig. 2 Various pretreatments for lignocellulosic biomass.

through covalent bonding with hemicellulose. Pretreatment to remove these amorphous polymers is essential to increase the specific surface area and crystallinity of cellulose.[28,29]

Two common types for pretreatment of this lignocellulosic material are fractionation and delignification. Fractionation is a technique to separate lignocellulosic biomass into cellulose, hemicellulose and lignin by disrupting biopolymer matrix to improve access to polysaccharides.[30] The purpose of delignification is the removal of lignin, but under some conditions some hemicellulose fraction is also separated along with lignin.[28,31,32] Usually delignification is included in the fractionation process to separate lignin for exposing cellulose to enzymatic hydrolysis.[32] Both of these techniques actually have the same purpose. In this review, lignocellulosic biomass pretreatment will be discussed as depicted in Fig. 2.

2.1. Physical pretreatment

As is well known, crystallinity of cellulose hinders the disruption of lignocellulose material. Size reduction is a usual step to disrupt biomass crystallinity. Several studies reported the influence of distribution of biomass particle size on its conversion to biofuel.[33–35] Size reduction increases the specific surface area of biomass and reduces the degree of polymerization and cellulose crystallinity; however it also depends on biomass characteristics.[36,37] On the other hand, power input for mechanical size reduction depends on the moisture content of biomass, initial and final sizes. Therefore, the specific energy consumption is also affected by particle size.[25,38–40] Suitable biomass particle size will obviously have impact on the design of handling, transportation and conversion facilities due to requirement of high efficiency of mass and heat transfer.[41–43] Liu *et al.*[44] studied the effect of steam explosion pretreatment on corn stover particle size for improving enzyme digestibility and reported that the amount of byproduct was higher and sugar recovery was lower for larger biomass particle size; however, sugar conversion and yield were higher during enzymatic hydrolysis. With the increase of particle size, specific surface area as well as crystallinity decrease.[44] Khullar *et al.*[45] studied the effect of particle size on enzymatic hydrolysis of pretreated *Miscanthus*. The highest total conversion of biomass was obtained by using the smallest particle size (0.08 mm), followed by the particle size of 2 mm, and the lowest conversion was achieved at particle size of 6 mm.[45]

Microwave irradiation is another method of physical pretreatment of lignocellulosic biomass. This pretreatment method has been improved over many years, and is well known for its high heating efficiency and easy operation. Ma *et al.*[46] investigated the rice straw pretreatment using microwave irradiation without the presence of any catalysts. The purpose of their study was to evaluate the influence of microwave irradiation on the recalcitrant structure, and their results showed that cellulose increased from 33.4% to 41.8%, while the acid soluble lignin decreased from 2.1% to 1.9%. This result indicates that microwave irradiation could disrupt the silicified waxy surface, break down lignin–hemicellulose complex, partially remove silicon and lignin, and expose more accessible surface area of cellulose.[46]

2.2. Chemical pretreatment

Utilization chemical substances to fractionate lignocellulose is widely known as pretreatment method with more advantages than physical pretreatment.[38,39] During chemical pretreatment, higher glucose yield can be obtained by removing hemicellulose or lignin.[47] Chemicals that are commonly used for this pretreatment[48–84] are summarized in Table 2.

For chemical pretreatment using alkaline or acid, lignin and hemicellulose removal is affected by pH. Alkaline pretreatment using NaOH usually gives higher lignin removal than acid pretreatment using HCl and H_2SO_4.[51,53,58,63,64] Alkaline pretreatment produces no by-product while acid pretreatment produced by-products such as 5-hydroxymethyfurfural and 2-furfuraldehyde.[48,51,66] Pretreatment using alkaline hydrogen peroxide begins to gain interest due to the advantage that lignin is degraded into oxygen and water and there is no residues left in the pretreated biomass.[48] In the alkali based pretreatment using NaOH, temperature only had minor impact on the lignin removal. It increased only 1% at same alkali dosage 7% w/v; but with increasing alkali dosage, the lignin removal increased from 41% to 72% at 140 °C.[50] Gu *et al.* reported that in low temperature pretreatment, the addition of a mixture of sodium carbonate and sodium sulfate prevented the degradation of carbohydrates.[65] Peracetic acid pretreatment also can remove lignin effectively and caused the degradation of some hemicellulose thus exposing cellulose.[64] In addition, both acid and alkaline pretreatments removed almost all carboxylic acid substitutions such as acetyl groups and uronic acids.[52] Chemical pretreatment process is widely used for industrial pulp and paper production.

Table 2 Effect and chemical substances of lignocellulosic biomass pretreatment

Chemical pretreatment	Chemicals	Effect	References
Alkaline	H_2O_2, NaOH, Na_2SO_3, Na_2S, lime ($CaOH_2$), Na_2CO_3, NH_4OH	High lignin removal, enrichment of holocellulose, increase the porosity of biomass and cellulose swelling	48, 50–53, 58, 61–67 and 77
Acid	H_2SO_4, peracetic acid, HCl	Remove hemicellulose fraction and increasing biomass crystallinity	49, 51, 52, 54–58, 62–64, 66 and 67
Ionic liquids	[Bmim][OAc], [bmim][Cl], [emim][OAc], [emim][CH_3COOH], [emim][$DEPO_4$], [dmim][$MeSO_4$], [amim][Cl], [DMSO/LiCl], [Bmpy][Cl]	Weaken the van der Walls interaction between cell wall polymers, disrupt arabinoxylan–lignin linkages, alter the fibrillar structure of cell wall, decrease cellulose crystallinity, increasing cellulose surface accessibility	49, 59 and 68–76
Organic solvent	Ethyl acetate, ethanol, acetic acid, formic acid	Break down internal lignin and hemicellulose bonds, increasing pore-volume and surface area of biomass	60, 61 and 78–80
Surfactant	Polyethylene glycol, Tween 80, Tween 20, sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DoTAB), Triton X-100, Triton X-114, Agrimul NRE 1205, HM-EOPO, amphoteric Anhitole 20BS, Neopelex F-25	Alter biomass structure, stabilizing enzyme, increasing interaction between holocellulose and enzyme, reducing adsorption of enzyme on lignin	81–84

Nowadays, ionic liquid (IL) is also known as one of the most promising green chemicals which can solubilize plant cell wall effectively at mild temperature.[49,85] IL is called as "designer solvents" due to immeasurable cation and anion combinations,[68] where the nature of cation and anion affects the solubility of biomass fraction and water interaction.[76,85,86] Recently, some researchers also paid attention on the use of ILs for lignin valorization. Through catalytic oxidation of lignin, valuable platform aromatic compounds were obtained.[87] Doherty *et al.* discussed the effect of anion composition on the efficacy of pretreatment between two ILs ([Bmim][OAc] and [Bmim][$MeSO_4$]), their result indicated that acetate anion removed >32% of lignin from maple wood flour and significantly reduced cellulose crystallinity. As a comparison, [Bmim][$MeSO_4$] only removed 19% of lignin without decreasing the crystallinity.[88] Pretreatment using ILs also played an important role on fiber size, and the later affected the solubility of lignocellulose in solvent.[70,88] Although the cost of pretreatment using ILs should be addressed carefully,[76,89] process efficiency of biomass pretreatment using ILs is still better than other available conventional processes. Since IL can be recovered easily, it can overcome cost problem in industrial application.[68,86,89]

Another attractive chemical pretreatment is organosolv process. This pretreatment is widely known for extracting lignin from biomass using organic solvents in the presence of acidic/alkaline catalyst. This process has been used in several chemical and fuel industries.[22,61,62,79,90,91] One of the advantages of this process is recovery of solvent is relatively easy, which can be conducted through various methods depending on solvent characteristics.[92,93] Lignin extracted using this process had high purity and contained a small amount of phenolic and aliphatic hydroxyl.[22,94,95] Without the presence of lignin, cellulose and hemicellulose fractions of the biomass can be effectively converted to platform chemicals such as 5-hydroxymethylfurfural (HMF) and levulinic acid (LA).[62,96] With this organosolv pretreatment process, the major fraction in lignocellulose can be utilized as raw material for valuable platform chemicals and biofuel, and the lignin fraction could be recovered for other applications. A number of solvents with various catalysts (acid, alkaline, and chloride salt) have been used (see Table 2) to improve the fractionation process.[97,98] In order to improve low recovery of hemicellulose and neutralization of acid/base, several studies reported the organosolv pretreatment of lignocellulosic materials without adding acid catalyst.[94–100] The use of NaOH (1.5% NaOH for 60 min) as the catalyst resulted in higher delignification efficiency than using sulfuric acid.[78] Wildschut *et al.*[101] investigated the influence of temperature, acid and ethanol concentration on the fractionation of wheat straw, and reported that these parameters played more important roles than reaction time and particle size. Without adding any catalyst, the delignification efficiency was 37.7% while the efficiency was 75.8% with the addition of acid (30 mM of H_2SO_4). Xylan recovery decreased dramatically from 71.8% to 4.7% as acid concentration was increased from 0 to 30 mM.[101] In the pretreatment of wheat straw, the use of organic acids gave better extraction of phenolic hydroxyl in lignin than voltaic alcohols in the degradation of hemicellulose and lignin.[80,102] Organosolv process is one of the common methods for delignification of wood in the pulp and paper industries. Most common used solvents are methanol, ethanol, formic acid and acetic acid. Often these solvents are used in combination with water.

Interestingly, some articles published reported that the addition of surfactant in lignocellulose fractionation can help improving enzyme digestibility.[81–84] Surfactant has amphiphilic structure that consists of hydrophilic head and hydrophobic tail. This structure of surfactant enables it to be adsorbed onto

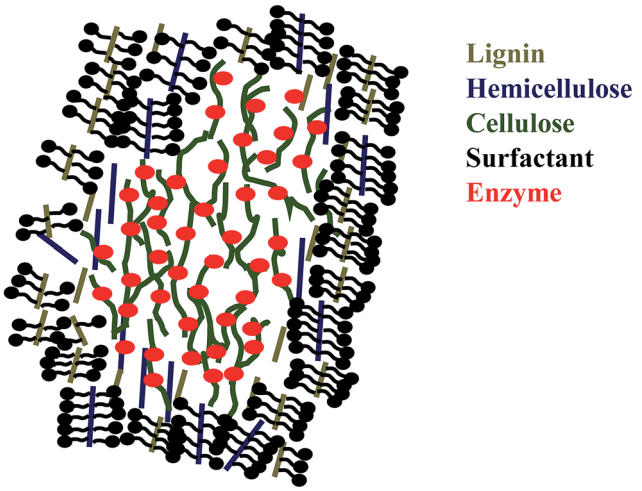

Fig. 3 Scheme of mechanism of surfactant in saccharification.

substrate thus modifies the structure of biomass.[103] Surfactant can modify the surface and interfacial energy in enzymatic hydrolysis which explains the increasing rate of enzyme hydrolysis.[103,104] There are five types of surfactant: non-ionic, anionic (negative charge), cationic (positive charge) and zwitterionic (positive and negative charges) and biosurfactant (produced by microorganism).[103,105] Several researchers reported that non-ionic surfactant gives better result in increasing hydrolysis rate than anionic or cationic surfactant.[81,84] Helle *et al.* observed that with the addition of surfactant, enzyme loading can be reduced. Qing *et al.* reported that reducing enzyme loading had greater impact on enzymatic hydrolysis.[81,104] It was said that non-ionic surfactant with high value of hydrophile–lypophile balance performed better in the degradation of lignin and hemicellulose, and anionic surfactant gave poor result in hydrolysis rate.[81,84,106] Surfactant in enzymatic hydrolysis was usually added at critical micelle concentration (CMC) where surfactant later formed micelle.[104] If the surfactant adding was above CMC, surfactant will interact with enzyme and reducing the effectiveness of enzyme.[104] The mechanism of how surfactant can increase saccharification (see Fig. 3) is that the hydrophobic part of surfactant binds with the hydrophobic part of lignin or hemicellulose and the hydrophilic part of surfactant prevents the unproductive enzyme binding with lignin, thus increases hydrolysis rate with a small amount of enzyme loading.[81,84]

2.3. Thermo-physical and -chemical pretreatment

Considering the environmental effect, an attractive pretreatment using water as the solvent has been used for lignocellulose fractionation. Water at elevated temperature and pressure, known as liquid hot water (LHW) can be used to hydrolyze lignocellulosic biomass.[107] Under high temperature and pressure, water dissociates into H_3O^+ and OH^- ions, which can act as acid or base catalyst. Several studies reported that LHW pretreatment resulted in lower hemicellulose (mannan and xylan) content in residual biomass due to accumulation of hydrogen ion and acetyl groups in hemicellulose which can act as acids to hydrolyze hemicellulose into sugars.[107,108] LHW is effective to separate xylans completely from glucans. After the separation, the major part that remains in the solid residue is glucose.[109] Yu *et al.* compared the pretreatments of biomass using HCl, NaOH and LHW and concluded that pretreatment using HCl and LHW resulted in the same solubilization of xylan (over 86%), while pretreatment using NaOH resulted in the highest removal of lignin. Despite the high need of energy in LHW, the residue after LHW pretreatment does not need washing, which is an advantage of the process.[110]

Steam explosion (SE) is also widely utilized for disrupting the structure of lignocellulosic materials. Generally, this pretreatment is always followed by microbial process to enhance cellulose accessibility.[111–114] Some researchers also did pre-impregnation with SO_2 or NaOH for better result after steam explosion; this impregnation was carried out in order to overcome non-uniformity and obtain deep penetration into biomass.[115,116] The impregnation with SO_2 was conducted to increase hemicellulose solubility[112–114] and NaOH impregnation to increase the removal of lignin during experiment.[115] Liu *et al.*[44] discussed the effect of corn stover particle size during SE pretreatment on improving the digestibility of enzyme. Their result indicated that larger particles size improved enzymatic hydrolysis performance and gave higher pretreatment efficiency. Adapa *et al.*[37] conducted grinding experiments on SE treated and untreated lignocellulosic materials in order to determine the effect of specific energy requirements on geometric mean particle size and distribution of lignocellulosic materials. They found that the SE pretreated biomass required less energy for grinding and particle size reduction of the untreated biomass needed considerable more energy and cost.[37,44] Wiman *et al.*[114] investigated the individual effects of pretreatment temperature, time, and sulfur dioxide uptake on cellulose accessibility. Their results concluded that cellulose accessibility increased with increasing pretreatment temperature and time. However SO_2 uptake had insignificant effect on cellulose accessibility but conversion of enzymatic hydrolysis increased almost 2 times.[114] This result agreed with that of Zimbardi *et al.* who mentioned that increasing acid loading did not show any significant improvement in water solubility but it greatly affected sugar partition between monomers and oligomers.[117] Pre-impregnation using acid can cause low recovery of C_5 sugar in the residue but can greatly improve enzymatic hydrolysis even though lignin content in the residue still remains high.

Pretreatment using ultrasound is considered as a promising technology in improving lignocellulosic material fractionation. In concept, ultrasound method utilizes cavitation to enhance heat and mass transfer during fractionation.[118,119] Bussemaker and Zhang mentioned that oxidizing radicals were produced during ultrasonification, and these radicals played important role in the disruption of the recalcitrant lignocellulosic material.[120] Several parameters in the ultrasound process such as frequency, particle size and stirring also influence the results of lignocellulosic material pretreatment (see Table 3).[121] Hemicellulose sugars are bound by glycosidic linkages and are accessible to chemical and physical treatment, while lignin can be separated by chemical treatment only.[120] Garcia *et al.* used ultrasound-assisted method

Table 3 Influences of frequency, particle size, biomass loading and stirring in ultrasound pretreatment[121]

Ultrasound pretreatment	
Frequency	• Higher frequencies can increase carbohydrate solubilization because of enhancing radical attack in consequence of increasing sonochemical effects • Lower frequencies are effective for delignification due to the enhanced accessibility from the physical effects of ultrasound such as pits and cracking
Particle size	• Decreasing particle size increases the carbohydrate solubilization and delignification • Decreasing pH with particle size because of hemicellulose dissolution
Biomass loading	•Greater delignification is achieved in the smaller solid loading of biomass
Stirring	• Improve fractionation of biomass (lower solid residue yield) • Increase radical production at low frequencies which resulted in lower percentage of remaining lignin

for the fractionation of olive tree pruning residues using three solvents (water, aqueous acetic acid and aqueous sodium hydroxide). Their results showed that higher yield and higher selectivity were obtained by using ultrasound than that without using ultrasound. For longer ultrasound time, sodium hydroxide solution gave better separation performance than other solvents.[118] The combination of ultrasound and addition of catalyst to liquefy lignocellulosic materials was studied by Kunaver *et al.*[122] They found that the use of ultrasound in the liquefaction process inhibited the formation of large molecular structures from degradation of lignin and cellulose.

Pretreatment of biomass in the presence of high pressure oxygen or air is called as wet oxidation. This process takes place at high temperature and effectively solubilizes hemicellulose fraction.[123] Arvaniti *et al.* investigated the effect of temperature, time and oxygen pressure in wet oxidation of rape straw and reported that pressure played more important role than temperature and contact time on cellulose and lignin recovery. By decreasing pressure, cellulose and lignin recovery increased, while decreasing temperature and contact time gave negative effect on lignin recovery.[124] Banerjee *et al.*[125] performed wet oxidation of rice husk with addition of Na_2CO_3. Their result agreed with that of Schmidt and Thomsen[123] in that most hemicellulose was dissolved and the solid fraction of biomass became black due to high pressure and temperature used in the process.[126] The purpose of adding sodium carbonate was to adjust the pH since pH is an important factor in biomass fractionation.[126] Kallioinen *et al.*[127] investigated wet oxidation of spruce, birch, and sugar cane bagasse using different alkaline agents (NaOH, KOH or $Ca(OH)_2$). Their result indicated that high removal of lignin was observed due to alkaline agent addition.[127]

One of the thermo-chemical pretreatments is the ammonia-based biomass pretreatment such as ammonia recycle percolation (ARP) and ammonia fiber/freeze explosion (AFEX). In AFEX pretreatment biomass and ammonia is enclosed in a high pressured reactor and the pressure is released rapidly to create an explosion effect. In ARP ammonia flows through biomass in the reactor and ammonia is recycled after the pretreatment.[38] Due to the difference in contact of ammonia and biomass, usually ARP results in low recovery of hemicellulose and high delignification, while AFEX results in low lignin removal.[38] These two processes are distinguished for their ability to enhance enzyme digestibility for the pretreated biomass which can reduce microbial need.[62,128] They are also classified as alkaline pretreatment which resulted in high selectivity towards lignin, especially for ARP which can remove significant fraction of hemicellulose and lignin.[38,126] The major parameters in these processes are reaction time, temperature, ammonia concentrations and loading.[124] Chundawat *et al.*[129] investigated the pretreatment of guayule using AFEX and reported that the pretreatment substantially improved overall enzyme digestibility by 4–20 folds. Kim *et al.*[130] studied the effect of temperature and time in the ARP pretreatment of rice straw. Higher temperatures with longer reaction times increased the hydrolysis of the internal lignin and hemicellulose bonds.[130] Similar result was also obtained by Bouxin *et al.*[131] who examined the effect of ammonia concentration in the ARP pretreatment and their results indicated that decreasing ammonia concentration reduced the solubility of lignin compound of poplar sawdust. Zhao *et al.* studied AFEX of corn stover with and without H_2O_2 as the catalyst and reported that the effect of temperature and reaction time was the same as that of ARP.[130,132] The addition of H_2O_2 in AFEX pretreatment was to increase lignin removal and sugar release.[132] Ammonia loading has negligible effect on xylan and lignin removal, but glucan content increased with increasing ammonia loading.[132] The increase of glucan content with ammonia loading was due to the increasing degradation of hemicellulose, removal of lignin and other soluble components.[132]

Supercritical CO_2 (SC-CO_2) is a potential thermo-physical pretreatment which is in principle similar to steam explosion. In supercritical condition, CO_2 has the characteristic of a nonpolar organic solvent with low viscosity and zero surface tension which can rupture the lignocellulose structure through penetration.[133] This method is usually paired with microbial attack because of vulnerable surface of biomass after SC-CO_2 treatment and no inhibitory product is reduced after the treatment.[134] Several parameters in the SC-CO_2 treatment have been studied thoroughly, such as temperature, pressure and time. Glucose yield tends to increase with the increasing of these parameters. However, glucose yield in SC-CO_2 treatment also depends on biomass characteristics.[133] In SC-CO_2 treatment, moisture content in biomass is an important factor because water can affect the penetration of CO_2, increasing moisture content results in higher sugar yield.[134,135] There are two explanations why higher moisture content gives higher sugar yield. Firstly, water and CO_2 at high pressure could form carbonic acid, which increases the acid hydrolysis of hemicellulose. Second: water enables the swelling of biomass that helps CO_2 penetrating deeper into the pores of biomass and disrupting biomass fibers through explosive release of pressure.[133,136]

2.4. Biological pretreatment

Biological pretreatment is the most expensive pretreatment method because of the high cost of certain microorganisms. Extensive studies on the use of microorganisms for pretreatment of lignocellulosic material have been conducted by various research groups, but the use of microbial for lignocellulosic material degradation is still far from industrial application. The main problem in the use of microbial process is the complex linkage of lignin–hemicellulose–cellulose, so combination with physical or chemical pretreatment is necessary before the microbial process.[16,137] Initial pretreatment such as steam explosion, supercritical CO_2, acid, alkaline, or organic solvent changes the physical and chemical properties of biomass which enhances enzyme digestibility. The change of biomass structure increases the digestibility of microbes due to polysaccharides modification. It should be noted that lignin removal must be carried out at low temperature to avoid sugar degradation.[137,138] Some researchers reported that it is important to remove lignin for ease of enzyme attack,[139] but it seems that it's not really the case. It is true that the complex linkage of lignin and carbohydrate hampers the enzyme digestibility of carbohydrate; therefore lignin needs to be removed for further conversion of lignocellulose into valuable chemical product. However some cases demonstrated that even though high lignin removal (>50%) was achieved but did not give high enzyme hydrolysis compared to low lignin removal pretreatment.[113,114,140] Hence, the most important in improving enzymatic digestibility is not high lignin removal but high cellulose

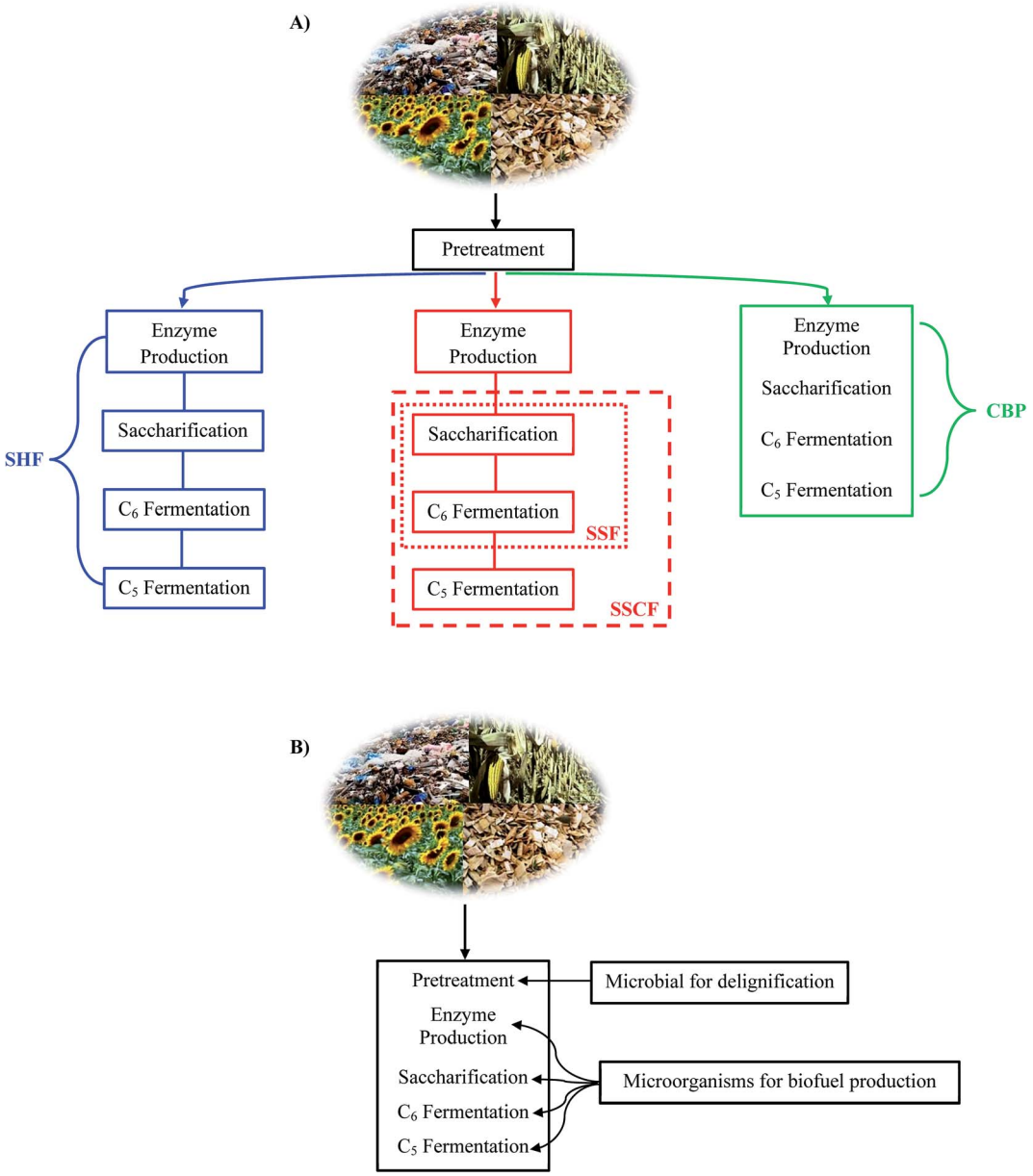

Fig. 4 (A) Schematic process for SHF, SSF/SSCF and CBP (B) schematic process for IBP.

accessible area. With high accessible area enzyme digestibility will also greatly increase.[141,142]

Process using microorganisms that can help removing lignin is known as biodelignification. Biodelignification can be carried out with the help of microorganism like fungi and bacteria. There are three main groups of fungus: white rot, brown rot and soft rot fungi. For bacteria there are four classes: actinomycetes, α-proteobacteria, β-proteobacteria and γ-proteobacteria.[138,143] These microorganisms can degrade lignin effectively even though the conversion is slow.[138,143–145] Among those microorganisms, the best one to degrade lignin effectively is white rot fungi because it exhibits highly oxidative enzymes.[146] On the contrary, brown rot fungi prefer to remove carbohydrate part with partially removed lignin due to different mechanism.[143] Soft rot fungi remove only soluble sugars from lignocellulose.[147] White rot fungi are known to produce ligninolytic enzymes such as lignin peroxides (LiP), manganese peroxides (MnP), versatile peroxides (VP) and laccase. LiP can actively degrade phenolic and non-phenolic part of lignin, MnP and laccase can directly oxidize phenolic unit but need mediator to digest non-phenolic unit, and VP is a hybrid of LiP and MnP that can oxidize both phenolic and non-phenolic part due to dual characteristic.[148,149] Brown rot fungi use Fenton oxidative reaction to generate hydroxyl radical (˙OH) and this radical will be used as an oxidant to attack lignin.[143,150] Lignin degrader bacteria have individual complex pathway for specific degradation of lignin components such as β-aryl ether, biphenyl, diarylpropane, phenylcoumarane and pinoresinol.[143] There are several important factors that can affect the effectiveness of fungi like fungal strain, cell wall of substrate and culture conditions.[151] Saha *et al.* observed the behaviors of 26 white rot fungal strains on corn stover and reported that inappropriate fungal strain and biomass combination will even result in carbohydrate loss without any lignin removal.[152] Except using fungi or bacteria to degrade lignin, enzyme delignification can also be considered since it offers the possibility to increase delignification efficiency and reduce process time.[148] Among the ligninolytic enzymes used for delignification, laccase is widely utilized for enzyme delignification due to high removal of lignin.[148] Using enzyme for delignification is easier than microorganism degradation because of wide ranges of optimum temperature and pH. The major factor is enzyme loading and solid to liquid ration in the process.[148] It should be also noted that using microorganisms for biomass pretreatment produces no inhibitor, thus it will greatly facilitate the next step such as saccharification or fermentation.[148]

There are four different combinations between thermochemical and biological treatments which are known as separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous and saccharification co-fermentation (SSCF), and consolidated bioprocessing (CBP) (see Fig. 4).[39,153,154] SHF has the advantage of optimizing sacchariffication and fermentation in separated process. SSF can produce high ethanol yield with low cost. SSCF is similar to SSF but the process from saccharification until fermentation of C_6 and C_5 sugar occurs simultaneously, hence results in low biofuel yield. CBP has the lowest capital cost but give the lowest yield of biofuel due to the presence of inhibitors which inhibit growth of microbes. Among these four processes, the most beneficial one is SSF since it requires low initial cost and can achieve high product yield.[39] IBP is a low cost process, however, the efficiency and the yield of this process are low.[39] Another process is called integrated bioprocessing (IBP). Unlike previous four processes whose pretreatments are either chemical or thermophysical, in this process every step including biomass pretreatment (delignification) uses microorganism and runs in a single reactor (see Fig. 4).[154,155] Therefore IBP at least needs 2 kinds of microorganism, one is for delignification and the other is for enzyme production until the fermentation step.[155] It is indeed true that IBP can greatly reduce total cost and especially there is no inhibitor formation due to microbial assisted delignification which make the subsequent step easier, but until now there are no reports about lignocellulosic biomass pretreatment and process by IBP.[155]

Biological pretreatment processes are affected by parameters such as pH, temperature and inhibitor (intermediate chemical: phenolic compounds, furan derivatives, weak acids).[156] The performance of several common microorganisms (*Cryptococcus curvatus*, *Trichoderma reesei*, *Rhodococcus opacus*, *Saccharomyces cerevisiae* and *Kluyveromyces marxianus*) for biological pretreatment in the presence of inhibitors has been studied by several research groups.[157–160] The most common inhibitors present in the pretreatment of lignocellulosic biomass usually are furfural, vanillin, *p*-hydroxybenzaldehyde (PHB), and syringaldehyde.[161] The existence of these inhibitors reduce the productivity of microorganisms.[157–160] Therefore, detoxification is necessary

Table 4 Removal of inhibitor for detoxification method[126]

Method	Removal of inhibitor	Note
Neutralization	Acetic acid, furfural and HMF	Poor ability to remove toxic compounds
Overliming	Furfural and HMF	Sugar loss due to hydroxide-catalyzed degradation reactions, no alter in acetic acid concentration
Adsorption	Furans, phenolic and acetic acid	Good removal of acetic acid and phenolic compounds
Ion exchange resin	Furans, phenolic and acetic acid	High removal of furan, total phenolic compounds and acetic acid
Electrodialysis	Acetic acid, furfural, phenolic compounds	Remove 90% of acetic acid, low sugar losses (<5%), environmental friendly, high instrument cost, better fermentability of the hydrolysate
Enzyme detoxification	Phenolic compounds	Excellent selectivity removal of phenolic content

Table 5 The effect of thermophilic bacteria in lignocellulose biomass pretreatment

Organism	Note
Clostridium thermocellum[165]	Degrade crystalline cellulose efficiently at 60 °C and produce a large multi protein complex called cellulosome, and increase ethanol tolerance and product yields
Caldicellulosiruptor saccharolyticus[165]	A suitable candidate for biohydrogen production, produce thermostable cellulolytic and xylanolytic enzymes, grow optimally at 70 °C on various kind of lignocellulose biomass
Caldicellulosiruptor bescii DSM 6725 (ref. 165 and 166)	The most thermophilic organism which grow efficiently with an optimum growth temperature of 80 °C, can degrade high concentrations of both unpretreated switchgrass and crystalline cellulose (up to 200 g L^{-1})

before further step in the biological process is carried out. There are several detoxification methods such as neutralization, overliming, adsorption, ion exchange, and enzymatic detoxification which have been used effectively to remove some inhibitors (see Table 4).[126] Subsequent process usually is conducted at mild temperature (20–37 °C) and pH 5–8, and these operation conditions sometimes can be a problem for scale-up in industrial application for some microorganisms.[162] Several microorganisms tolerant to extreme media (low/high temperature or pH and inhibitor) have been developed during the past decades in order to improve the cost efficiency of biomass-based biofuel processes.[163,164] Several microorganisms which have thermostable or thermophilic behavior have been studied to degrade lignocellulosic materials. These microorganisms offer some advantages such as shorter hydrolysis time, high resistance in low or high pH, decreasing risk of contamination and low cost of energy.[165] Thermophilic bacteria also have gained much interest especially for CBP (high temperature decreases the chances of contamination) and SSF (shorter hydrolysis time which decreases potential contamination). A few examples of thermophilic bacteria that were used in the processes can be seen in Table 5.[165,166]

3. Production of valuable chemical product

Many reviews have already discussed about utilizing lignocellulose biomass to produce biofuel. In this review, the authors will focus and discuss on the steps to produce valuable chemical products from the pretreated lignocellulose including biofuel, chemicals and advanced materials.

3.1. Biofuel

Lignocellulose material can be converted into several kinds of biofuel such as biogas/syngas, biohydrogen, bio-oil, and bio-ethanol. Biogas and syngas have the same components (CO_2, CH_4, H_2 and N_2) but the process which produces them are different. Biogas is produced from the microbial assisted process and syngas is created by the partial combustion of biomass (gasification).[18,167] Production of biogas is conducted by anaerobic digestion (AD), which has complex mechanism. There are four crucial steps in AD: hydrolysis, acidogenesis, acetogenesis and methanogenesis.[168] Hydrolysis is always the first step in the microbial assisted process in order to break down the complex oligomers of lignocellulose.[168] Acidogenesis is the fermentation step to create acidic pH while breaking down the organic matter.[169] Acetogenesis is the process of acetogens that creates acetic acid, CO_2 and H_2O.[169] The last step is methanogenesis. There are two general pathways to create methane:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ (from acidogenesis)} \quad (1)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \text{ (from acetogenesis)} \quad (2)$$

Although there are two reaction mechanisms that can create methane, the main reaction is the 2nd one.[169] There are at least three kinds of bacteria needed in AD, they are for acidogenesis, acetogenesis and methanogenesis.[170] Syngas is produced by biomass gasification which in principle is similar to coal gasification except that biomass gasification occurs at lower temperature due to more reactive feedstock.[171] In biomass gasification, basically there are three types of process: pyrolysis, partial oxidation and steam reforming.[172] Pyrolysis is the thermal anaerobic decomposition of biomass at elevated temperature. Partial oxidation consumes less than the stoichiometric amount of oxygen needed, and steam gasification involves the reaction of water with biomass.[171,172] Typical assumed reactions of these processes can be seen in Table 6 (based on cellulose fraction).[172] Particularly biomass gasification usually involves the following steps: drying, pyrolysis, biochar gasification and combustion.[173] Drying is necessary in order to reduce the moisture content of biomass. After that pyrolysis occurs for thermal breakdown of biomass. At this stage many products are produced such as tar, bio-oil and biochar that will be discussed further.[173] Biochar gasification involves the following reactions between biochar and gas evolved during the process:

Table 6 Stoichiometric reactions of pyrolysis, partial oxidation and steam gasification (adapted from Klass[172])

Process	Stoichiometry	Enthalphy (kJ g^{-1} mol^{-1}) $T_{ref} = 1000$ K
Pyrolysis	$C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C$	209
	$C_6H_{10}O_5 \rightarrow 4CO + CH_4 + C + 2H_2 + H_2O$	−16
	$C_6H_{10}O_5 \rightarrow 3CO + CH_4 + 2C + H_2 + 2H_2O$	−152
Partial oxidation	$C_6H_{10}O_5 + 0.5O_2 \rightarrow 6CO + 5H_2$	96
	$C_6H_{10}O_5 + O_2 \rightarrow 5CO + CO_2 + 5H_2$	−180
	$C_6H_{10}O_5 + 1.5O_2 \rightarrow 4CO + 2CO_2 + 5H_2$	−464
Steam reforming	$C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2$	322
	$C_6H_{10}O_5 + 3H_2O \rightarrow 4CO + 2CO_2 + 8H_2$	276
	$C_6H_{10}O_5 + H_2O \rightarrow 4CO + CO_2 + CH_4 + 4H_2$	85

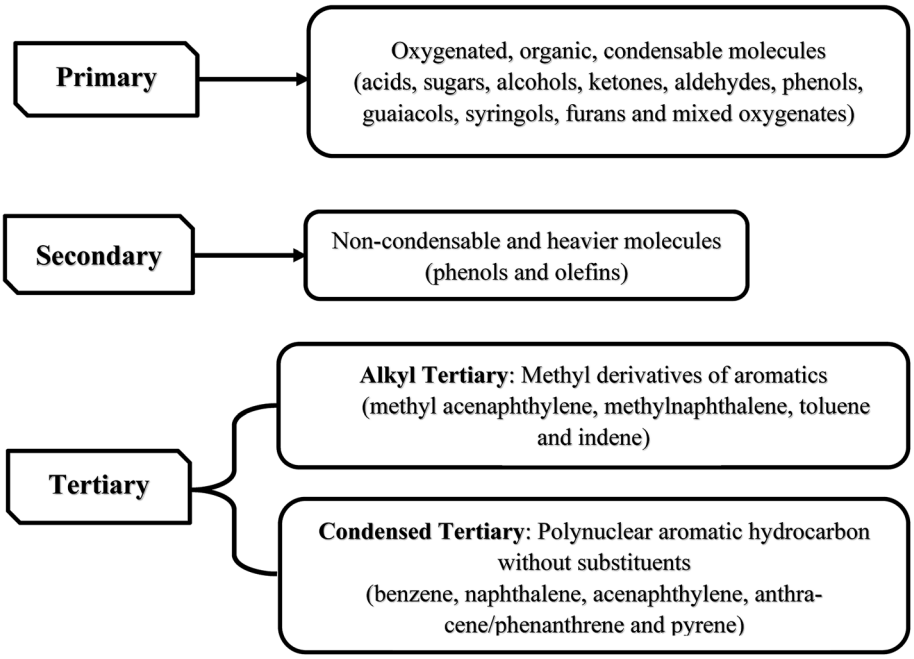

Fig. 5 Major groups of tar.

$$\text{Biochar} + O_2 \rightarrow CO \text{ and } CO_2$$

$$\text{Biochar} + CO_2 \rightarrow CO$$

$$\text{Biochar} + H_2O \rightarrow CH_4 \text{ and } CO$$

$$\text{Biochar} + H_2 \rightarrow CH_4$$

Combustion is almost the same as biochar gasification, but it mainly involves O_2 to create CO_2 and CO as products, the reaction is exothermic.[173]

Pyrolysis can produce bio-oil and other products such as biochar, tar and gases. Biochar, a solid product from pyrolysis, consists mainly of carbon (~85%).[173] Tar and bio-oil, liquid product generated in the process, is an undesirable product which is formed at 200 to more than 500 °C. There are three major groups of tar composition (see Fig. 5).[173] Bio-oil is produced by rapid and simultaneous depolymerization of major components in lignocellulose whose compounds generally consists of hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids and phenolic compounds.[173] Gases resulted from pyrolysis are divided into two groups: condensable gas (made of heavy molecular weight components, condense upon cooling) and non-condensable gas (lower molecular weight like CO_2, CO, CH_4, C_2H_6 and C_2H_4 that do not condense on cooling).[173] Based on heating rate, pyrolysis can be classified as slow and fast pyrolysis. Although pyrolysis is an anaerobic process, sometimes it is conducted in the presence of medium such as water (hydrous pyrolysis) and hydrogen (hydro pyrolysis) to produce some chemicals. Based on vapor residence time, slow pyrolysis is divided into carbonization and conventional and fast pyrolysis is categorized as flash and ultra-rapid (Table 7).[173–177] From thermal standpoint, pyrolysis can be divided into four stages: (1) drying (~100 °C), (2) dehydration (100–300 °C), (3) primary pyrolysis (>200 °C) and (4) secondary cracking (~300–900 °C).[173] In the beginning, biomass is dried to remove free moisture.[173] After that, dehydration of biomass occurs with the release of water and low molecular weight gases.[173] In primary pyrolysis, most vapors or precursors of bio-oil and decomposition products of large biomass molecules (char, condensable and non-condensable gases) are produced.[173] In the final stage (secondary cracking) large condensable gases with molecular weight are cracked to form additional char and gases.[173]

There are five different strategies to produce bioethanol; they are SHF, SSF, SSCF, CBP and IBP as previously mentioned in Section 2.4. Among the steps in these processes, the key to produce bioethanol is fermentation. Generally, fermentation is known as the process to convert sugars into acids, alcohols or gases.[178] There are two kinds of fermentation, C_6 and C_5 fermentation. Hexose fermentation starts with glycolysis where sugar is decomposed into pyruvate, then pyruvate is transformed by two kinds of enzyme (pyruvate decarboxylase and alcohol dehydrogenase) to produce ethanol and CO_2.[179,180] The reaction of hexose fermentation is depicted in Fig. 6.[180] Pentose fermentation by recombinant *S. cerevisiae* was studied by several researchers. It is said that *S. cerevisiae* cannot digest xylose and arabinose but can ferment their isomer D-xylulose.[180] Hence, gene encoding bacteria (xylose isomerase) or fungi (xylose reductase) which has the ability to utilize xylose and arabinose to produce D-xylulose is introduced into *S. cerevisiae* to improve pentose fermentation.[180] Complex reaction mechanism of pentose fermentation by recombinant *S. cerevisiae* was well discussed by Hanh-Hägerdal.[181]

Table 7 Types of pyrolysis

Based on	Pyrolysis process	Residence time	Major products
Heating rate	Slow[174]	Days	Biochar
	Fast[175]	<2 s	Bio-oil
Medium	Hydrous pyrolysis (H_2O)[176]	45 min	Gases (CO and CO_2)
	Hydropyrolysis (H_2)[177]	<2 min	Bio-oil
Vapor residence time[173] (slow pyrolysis)	Carbonization	Days	Biochar
	Conventional	5–30 min	Biochar, bio-oil, gas
Vapor residence time[173] (fast pyrolysis)	Flash	<1 s	Bio-oil, chemicals, gas
	Ultra-rapid	<0.5 s	Chemicals, gas

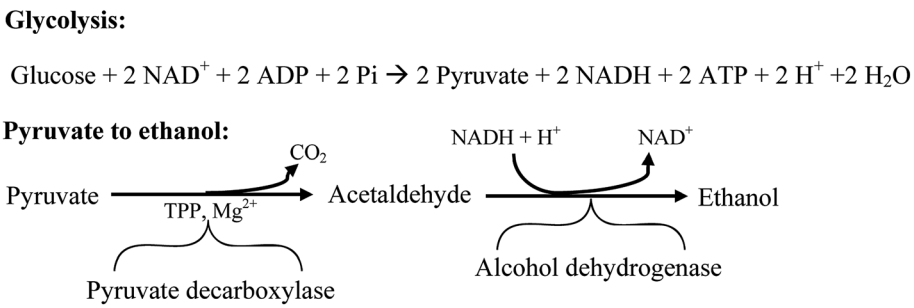

Fig. 6 Reaction mechanism in hexose fermentation.

Biohydrogen ($BioH_2$) can be produced *via* thermochemical (gasification and pyrolysis) or biological routes.[182] For production of H_2 through pyrolysis, it can be achieved directly by fast or flash pyrolysis, while gasification can be used to produce H_2 through partial oxidation and steam reformation, then further improved by water–gas shift reaction.[182] The mechanism of pyrolysis and gasification can be seen in the previous paragraph. *Via* biological routes, there are two classifications of process using biomass as a source to produce $bioH_2$.[183] They are light dependent (photo fermentation) and light independent (dark fermentation) which have completely different mechanisms.[184] Photo-fermentation uses photosynthetic bacteria which produce nitrogenase enzyme to produce H_2 with the help of solar energy. The key to produce $bioH_2$ in this process is that nitrogenase has the ability to use magnesium adenosine triphosphate and electrons to consume substrate (glucose is chosen as the precursor to represent biomass):[185]

$$C_6H_{12}O_6 + 6H_2O \rightarrow 24H^+ + 6CO_2 + 24e^- \rightarrow 12H_2 + 6CO_2$$

Dark fermentation (DF) is a process to convert biomass to $bioH_2$ using anaerobic bacteria without light source. The common reactions during DF by facultative anaerobic microorganism are:[186]

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (3)$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (4)$$

$$4C_6H_{12}O_6 + 2H_2O \rightarrow 3CH_3CH_2CH_2COOH + 2CH_3COOH + 8CO_2 + 10H_2 \quad (5)$$

Theoretically, DF can achieve maximum yield of 4 moles H_2 per mole hexose if the reaction produced only acetic acid (reaction (3)) and 2 moles H_2 for butyric acid production (reaction (4)). However this situation cannot occur since the result always contains both acetic acid and butyric acid (5).[182,187] Some researchers mentioned that the combination of DF and photo-fermentation can increase H_2 yield since the formation of organic acid is unavoidable in DF, because photo-fermentation prefers volatile fat acids (VFA) as the substrate to sugars.[188,189] According to the following reactions, a theoretical maximum yield of 12 moles H_2 per mole hexose can be achieved by the combination of DF and photo-fermentation:[189]

Stage 1 (DF): $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$

Stage 2 (photo-fermentation): $2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2$

Based on the bacteria used in DF, there are three different reaction mechanisms.[185] In fermentation, it always begin with glycolysis of carbohydrate to form pyruvate, after that it will be separated in three different steps to form $bioH_2$ based on three kinds of bacteria. The first using facultative anaerobes in which pyruvate will be converted into acetyl-CoA and formate by pyruvate formate-lyase (PFL) (a) then H_2 and CO_2 are generated through break down of formate by formate hydrogen lyase complex (b).[185] The second pathway using obligate anaerobes in which pyruvate is oxidized into acetyl-CoA and CO_2 through the reduction of ferredoxin (Fd) by pyruvate ferredoxin oxidoreductase (c), then the reduced ferredoxin (Fd(red)) is re-oxidized

and oxidized ferredoxin (Fd(ox)) is regenerated by [Fe–Fe] hydrogenase (HydA) together with the production of H_2 (d).[185] The third pathway is by thermophilic bacteria in which pyruvate formation generates NADH that reduces Fd(ox) by NADH-ferredoxin reductase (NFOR) (e), then Fd(red) generates H_2 using enzyme HydA (f).[185]

$$\text{Pyruvate} + \text{CoA} \rightarrow \text{acetyl-CoA} + \text{formate} \quad \text{(a)}$$

$$\text{Formate} \rightarrow H_2 + CO_2 \quad \text{(b)}$$

$$\text{Pyruvate} + \text{CoA} + 2\text{Fd(ox)} \rightarrow \text{acetyl-CoA} + CO_2 + 2\text{Fd(red)} \quad \text{(c)}$$

$$2H^+ + 2\text{Fd(red)} \rightarrow H_2 + 2\text{Fd(ox)} \quad \text{(d)}$$

$$2\text{NADH} + 4\text{Fd(ox)} \rightarrow 2\ NAD^+ + 4\text{Fd(red)} \quad \text{(e)}$$

$$4H^+ + 4\text{Fd(red)} \rightarrow 2H_2 + 2\text{Fd(ox)} \quad \text{(f)}$$

3.2. Chemicals

3.2.1. From carbohydrate. The simplest chemical building block derived from carbohydrate is furan molecules such as furfural and 5-hydroxymethylfurfural (HMF), which can be produced through acid catalyzed dehydration of C_5 and C_6 sugars.[190] Many catalysts have been used in order to improve the yield of HMF and furfural either using homogenous (mineral, organic acid and ionic liquid) or heterogeneous catalyst (zeolite, metal salt, polyoxometalates and resins).[191,192] Hydrogenation of furfural will result in furfuryl alcohol, 2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF) that have applications in polymer industry and as potential fuel.[193,194] The very famous HMF derivative is 2,5-furandicarboxylic acid (FDCA) which can be obtained through oxidation. This compound has emerged as a potential substitute for petroleum-derived terephthalic acid used in manufacturing poly(ethylene terephthalate) (PET) that is usually used for making plastic bottle and clothing.[195–197] The other HMF derivative, (2,5-dimethylfuran) with high octane number and energy density, has the potential to replace gasoline directly.[196,198] DMF can be produced from hydrogenation of HMF and subsequent hydrogenolysis.[198,199] Hydrogenolysis of HMF to DMF means the cleavage of C–O by hydrogen with the help of catalyst.[198,199] Levulinic acid (LA) is another derivative from HMF that is obtained through acid rehydration. It can be further upgraded in many sectors of industry such as fuel additives, polymer and resin.[18,195,200]

Other chemicals such as sorbitol and xylitol can be obtained through the hydrogenation of hexose and pentose in the presence of catalyst.[201–203] Glycerol is widely utilized in industry as the building block for making bio-solvents, cosmetics, batteries, polymers and surfactants.[197] This substance can be produced from sugars by simultaneous hydrogenation and hydrogenolysis, or by direct hydrogenolysis of sugar alcohols (sorbitol and xylitol).[204–207] Hydrogenolysis in this process is defined as hydrocracking of carbon chain that leads to the formation of shorter polyos/alcohols. Actually this process is almost similar to hydrogenation except the addition of base promoter in order to catalyze the C–C cleavage of dehydrogenation intermediate products (retro aldol derived sugars).[207–210] The formation of glycerol resulted in higher yield *via* hydrogenolysis of sugar alcohol than sugar. In this process other glycols were also formed such as ethylene glycol (EG) and polyethylene glycol (PG).[205,206]

Apart from thermochemical conversion, there are two products produced by microbiology conversion: lactic and succinic acid. Microbial sources to produce lactic acid is mainly from bacteria (*Bacillus* sp., *Streptococcus* sp., *Lactobacillus* sp.) and mold (*Rhizopus* sp., *Mucor* sp., *Monilia* sp.).[180,211] There are two kinds of fermentation of lactic acid, homo-fermentative and hetero-fermentative.[211] In homo-fermentative, carbohydrate from lignocellulose biomass is converted by the Embden Meyerhof Parnas (EMP) glycolysis pathway that produces pyruvate and later microorganism produces lactic acid as the single product by lactate dehydrogenase.[180,211] For hetero-fermentative, not only lactic acid but other minor products also appear such as ethanol, diacetyl, formate, acetoin or acetic acid and CO_2.[211] There are two mechanisms in hetero-fermentative: bifidus and 6P-gluconate pathway, both pathways utilize phosphoketolase enzyme to generate lactic acid from sugars with complex reactions that were discussed by Kandler.[212]

Unlike the previous fermentation that pyruvate is the key reactant, succinic acid is synthesized firstly through glycolysis but pyruvate will not be used to form succinic acid; it is phosphoenol pyruvate (PEP) that will be the key to form succinic acid.[213–215] The reaction mechanism of producing succinic acid is very complex and depends on bacterial or fungal type used in the process. Several kinds of bacteria that have been thoroughly studied are *Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, *Mannheimia succiniciproducens* and recombinant *Escherichia coli*.[180,213] All these bacteria form mixed acid fermentation that produces a mixture of products including succinic acid, ethanol, lactic acid, formic acid and acetic acid; from which succinic acid must be separated.[180] For *A. succinogenes* and *A. succiniciproducens*, they form succinate acid *via* PEP carboxykinase pathway using four key enzymes: PEP carboxykinase, malate dehydrogenase, fumarase and fumarate dehydrogenase.[214] In *M. succiniciproducens* there are seven key enzymes (PEP carboxykinase/carboxylase, pyruvate kinase, oxaloacetate decarboxylase, malate dehydrogenase, malic enzyme, fumarase and fumarate reductase) to produce succinate.[213] While recombinant *E. coli* has six different pathways with PEP carboxykinase plays the minor role, which causes lower yield of succinic acid production.[213] Interestingly, the PEP carboxykinase pathway in bacteria fermentation is adjusted by CO_2 level where higher CO_2 level will produce higher yield of succinic acid.[213,214] The industry application of succinic acid is huge, especially in these four markets: surfactant/detergent extender/foaming agent, ion chelator, food market (acidulant/pH modifier, flavoring agent, anti-microbial agent) and health related agent.[214] The development of these chemical building blocks is very advanced now due to dwindling supply of petroleum oil and climate change problem that haunted future generations on earth.

3.2.2. From lignin. In the past, lignin isolated from the pretreatment of lignocellulose is usually utilized to generate heat and steam in industrial process. Lignin has potential industrial applications since it is abundant in phenolic compounds which are composed of high molecular weight alkylphenol units.[216] Valuable chemical products that usually come from lignin are phenolic compounds which are classified into several types: *p*-hydroxyl, vanillyl, syringyl and cinnamyl.[217] Many works investigated the utilization of lignin to produce valuable chemical products in order to find a suitable process at reasonable cost for establishing industrial scale lignin valorization. There are many routes to convert lignin to phenolic such as liquefaction,[218] oxidation,[219] hydrolysis,[220] hydrocracking[216] and solvolysis.[221] All these methods are based on the concept of depolymerization. The mechanisms of lignin depolymerization are different, and depend on the route used. At the end, complex oligomer molecules will be broken down into simpler molecules such as phenols, aldehydes, aromatics and ketones which have many applications in industry.[222] Thermal degradation of lignin under harsh condition usually results in a range of products composed mainly of simple aromatics, while depolymerization *via* oxidation produces low molecular weight phenolic compounds.[219,222] In lignin depolymerization, catalyst is always required to assist selective bond cleavage. Catalysts that have been used for this purpose include alkaline agent (KOH and NaOH) for base catalyzed depolymerization, zeolites, amorphous silica–alumina, metal salt and noble metal.[223] The most valuable phenolic compound from lignin is vanillin which has good prospect in polymer industry to replace petroleum based materials like styrene and terephthalic acid.[224] Purification of vanillin from lignin depolymerization is difficult, but it is important to get high purity vanillin as a high value product. Separation and purification methods such as extraction, distillation, crystallization, membrane separation and adsorption have been studied to obtain highly purified vanillin, however these processes are usually energy intensive and environmental unfriendly.[224,225] The overall reaction mechanism of chemicals from lignin and carbohydrate is shown in Fig. 7.

3.3. Advanced material

Apart from bio-fuels and chemicals, lignocellulose biomass can also be utilized for environmental remediation and development of advanced materials such as adsorbent, nanocomposites; for energy storage, transportation, medical application in drug delivery and biosensing.[226–230] A few works reported using lignocellulose-based material as biosorbent for heavy metal or dye removal.[227,231] Adsorption using biosorbent is not restricted by physical bonding, it may involve strong interaction between sorbent and solute molecules.[232] Lignocellulose biomass can be utilized directly for adsorption or chemically modified (commonly using base or acid) to enhance adsorption capacity.[231] In general, chemically modified biosorbent has better adsorption performance due to formation of new functional group that creates more active binding sites.[231]

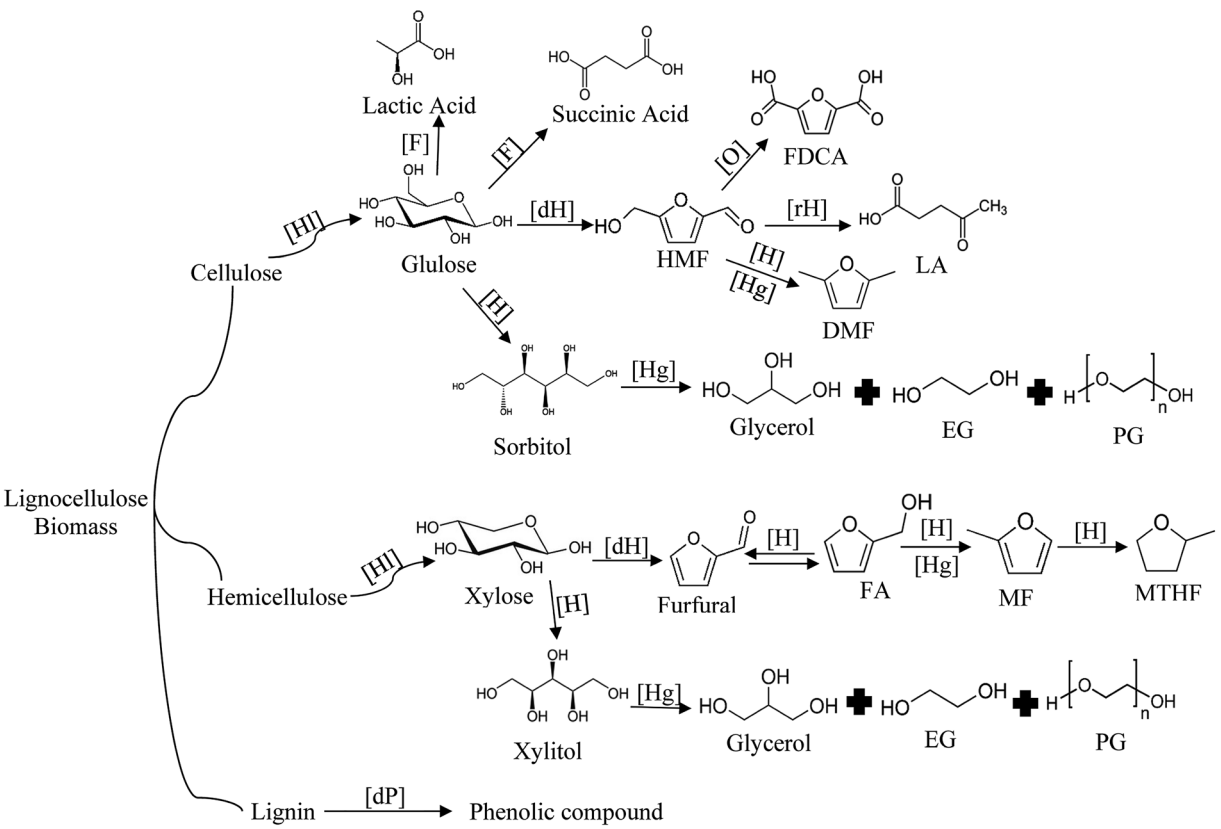

Fig. 7 Overall reaction mechanisms of lignocellulose to chemicals. F: fermentation, Hl: hydrolysis, dH: dehydration, rH: rehydration, O: oxidation, H: hydrogenation, Hg: hydrogenolysis, dP: depolymerization.

Electric double layer capacitor (EDLC) or supercapacitor is an energy storage device. It uses carbon as the active material which can be derived from lignocellulose biomass.[226] Supercapacitor from lignocellulose can be created by the hydrothermal carbonization (HTC) process which is classified into high temperature and low temperature HTC.[233] High temperature HTC (>300 °C) usually produces carbon nanotubes, graphite and activated carbon materials, while low temperature HTC (<300 °C) produces various carbonaceous materials with different sizes and shapes.[233]

Several works reported producing supercapacitors from lignocellulose biomass such as cornstalk, spruce, corncob, cassava peel, water hyacinth.[226,234–237] Wang *et al.* converted cornstalk into porous graphitic carbon nanosheets by pyrolysis at high temperature (1000 to 1200 °C).[226] Kurniawan *et al.* produced carbon microsphere from water hyacinth using subcritical water instead of pyrolysis, which is known as an environmental friendly method.[236] Several reaction mechanisms can occur in the HTC process such as hydrolysis, dehydration, decarboxylation, polymerization and aromatization.[238] These reactions did not occur consecutively, but appeared as a parallel network of different reaction paths that primarily depend on the type of feed.[238]

Besides supercapacitors, HTC process also produces another product called carbon fiber. Conventionally the precursor used in carbon fiber production is lignin isolated from lignocellulose biomass. Usually lignin obtained from lignocellulose biomass pretreatment is purified, then processed using several processes such as spinning, thermostabilization and carbonization to generate carbon fiber.[239] Soenjaya *et al.* produced carbon fiber from water hyacinth through pyrolysis. Tar from pyrolysis was extracted to obtain phenolic compounds. These phenolic compounds then were utilized as the raw material for producing carbon fiber.[240]

Cellulose is the most abundant renewable polymer in the world. For hundreds of centuries it has been used as sources for energy, textile and building materials.[228] This natural polymer can be used as the raw material for producing nanoscale material known as nanocrystalline cellulose (NCC). NCC has a diameter of 5–70 nm and a length between 100 and 250 nm. It exhibits extraordinary properties such as high tensile strength (7500 MPa), high rigidity (100–140 GPa) and large surface area (150–250 $m^2\ g^{-1}$).[230] Due to these remarkable properties, NCC is considered as one of the strongest and stiffest materials in the world.[230] Cellulose is also utilized as the raw material for cellulose nanofibrils (CNF) and cellulose microfibrils (CMF) production.[241] Both of these materials contain amorphous and crystalline parts of cellulose.[228] CNF has nanoscale diameter like NCC, but microscale length.[242] There are several ways to obtain CNF, using either mechanical or chemical treatment. For mechanical treatment, techniques commonly used are homogenization, cryocrushing, grinding and microfluidization. The main purpose of these processes is to defibrillate fibers.[243,244] Combination of enzymatic or chemical hydrolysis with mechanical treatment also has been used in order to reduce high energy consumption of mechanical treatment.[245,246] Ultrasonication also has been used to isolate CNF. This process uses acoustic cavitation to induce microjets and shock waves on microfibers. Thus, it can break the van der Waals molecular interactions among nanofibers.[247]

Generally, there are two steps to produce NCC from cellulose fiber: hydrolysis of the amorphous region of cellulose fiber and fragmentation of crystalline part to produce NCC.[248] Acid hydrolysis is employed to remove amorphous part of cellulose. Sulfuric acid is commonly used for acid hydrolysis under strictly controlled conditions of temperature, agitation, time and acid to cellulose ratio.[249] The types of acid used is very important in NCC preparations. Besides sulfuric acid hydrochloric acid also has been used to hydrolyze cellulose fiber, but resulted in flocculating aqueous suspensions.[228,249] In contrast, sulfuric acid as hydrolyzing agent introduces sulfate ions onto hydroxyl groups that prevents aqueous suspensions from agglomeration.[250] Normally, rod-like nanocrystal morphology were obtained by using either hydrochloric or sulfuric acid.[249] Combining sulfuric and hydrochloric acid under sonication will give spherical NCC with better thermal stability than rod-like shaped NCC.

Oxidation using ammonium persulfate is believed to give more homogeneous NCC than acid hydrolysis.[230] Post treatment like mechanical or sonication is conducted after acid hydrolysis in order to disperse nanocrystals into a stable suspension.[228] Drying is an important step in NCC/NCF preparation. Due to the hydrophilic nature of cellulose, hydrogen bonds of cellulose tend to aggregate forming bulky material that spoils the nanostructure material.[228,251] Therefore, other drying methods usually considered are freeze-drying, supercritical drying or spray drying to keep the nanoscale dimension of CNF or NCC.[252]

4. Concluding remarks

The main purpose of using lignocellulosic biomass as raw material for biofuels and chemicals production is that it is renewable and environmental friendly. Success of the process strongly depends on the pretreatment method used to remove lignin from cellulose or hemicellulose. To the present, various methods are available for the pretreatment of lignocellulosic material and these pretreatment methods are categorized as physical, chemical, thermophysical, thermochemical and biological pretreatment.

Chemical pretreatments require chemical substances to extract lignin from the structure of lignocellulosic material, and most chemicals used will end up as waste which need further treatment prior to its release to environment. Thermophysical and thermochemical pretreatments are mostly conducted at high temperature and high pressure, and often the addition of chemical substances as catalyst is needed. In terms of cost and complexity of process, thermophysical and thermochemical pretreatment processes are expensive. Since thermophysical and thermochemical pretreatments are operated at pressure between 10 and 50 bar and temperature between 100 and 250 °C, special design and material of construction for delignification reactor are required. These become the main obstacle for biofuels and chemicals production in large scale.

Although development in biological treatment of lignocellulosic material has improved considerably, some considerations are still needed before it can be implemented in industrial scale. Factors such as oxygen supply (low gas solubility at elevated temperature), existence of inhibitors, energy

consumption, economy value, waste production and growth of microorganism need to be considered. Deep and comprehensive studies are still required in order to make the biological pretreatment viable for industrial scale in terms of efficiency of energy and cost.

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