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Lignin utilization: A review of lignin depolymerization from various aspects

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ABSTRACT

Lignin is the most abundant aromatic polymer in nature. Due to its high amount of phenolic compounds storage, lignin is considered as an alternative source for various polymers and biomaterials production. Except for the native lignin in lignocellulose, a massive amount of technical lignin is being produced daily all over the world. However, the complex structure and low reactivity of lignin limit its further applications and currently, most of the lignin is burned for generating energy. Therefore, the depolymerization of lignin is considered one of the important challenges in lignin utilization. Methods for lignin depolymerization can be divided into thermochemical treatment, mechanical treatment, chemical catalysis, and biological treatment. Different methods for lignin depolymerization, their characteristics and products are extensively discussed in this review.

1. Introduction

Due to the massive consumption of fossil fuel and its limited storage, alternative energy and chemical sources are urgently needed. Thus, using natural plant resource, lignocellulose, to produce bioethanol and energy has become a hot topic in various areas. One of the major methods to produce bioethanol is converting the cellulose and hemicellulose in the lignocellulosic materials. However, a large amount of lignin could be left as a by-product after the bioethanol production due to its low reactivity and marketing value [1]. Furthermore, lignin is also considered as a by-product in the pulping industry. Thus, besides converting cellulose to valuable products, converting lignin to other value-added products also attract various research attention.

Lignin is the most abundant natural phenolic polymers in the world. In nature, lignin polymer usually forms ether or ester linkages with hemicellulose which is also associated with cellulose. Therefore, these nature polymers construct a complicated and valuable lignocellulose polymer (Fig. 1). Different sources of lignocellulose contain different ratios of these constructive polymers. In hardwood stem, the xylem usually contains 40–55% of cellulose, 24–40% of hemicellulose and 18–25% of lignin, while the softwood stem contains 45–50% of cellulose, 25–35% of hemicellulose and 25–35% of lignin [2].

Lignin has a complicated cross-linking structure and contains several functional groups within the molecule, including aliphatic hydroxyl, phenolic hydroxyl and methoxyl groups. These functional groups affect the reactivity and chemical properties of lignin, especially the hydroxyl groups and aromatic structure are the most critical functional groups to determine the characteristics of the polymers [3,4]. The aliphatic hydroxyl group usually is the most abundant hydroxyl group in lignin polymer. However, the ratios of these hydroxyl groups in different sources of lignin could be various [1].

The three major precursors of the lignin polymer are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Fig. 2). Lignin from different plants is constructed by various percentages of these precursors. For instance, the lignin from softwood mainly contains coniferyl alcohol, around 90–95%, while the lignin from hardwood usually contains coniferyl and sinapyl alcohols, around 25–50% and 50–75%, respectively, and the lignin from grass typically contains all three

List of abbreviation: HBT, 1-hydroxybenzotriazole; ABTS, 2, 2′-azinobis (3 - ethylbenzothiazoline - 6-sulphonic acid); 5CVA, 5-carboxyvanillic acid; DDVA, 5, 5′-dehydrodivanillate; ATP, Adenosine triphosphate; GS-HPV, α-glutathionyl-β-hydroxypropiovanillone; ALDHs, Aldehyde dehydrogenases; Al_2O_3, Aluminum oxide; HPV, β-hydroxypropiovanillone; CsOH, Cesium hydroxide; $Ca(OH)_2$, Calcium hydroxide; *C. echinulata*, *Cunninghamella echinulata*; DyP, Dye-decolorizing peroxidase; FeSO4, Ferrous sulfate; FeS, Ferrous sulfide; GSH, Glutathione; HPLC, High performance liquid chromatography; HPVZ, HPV oxidase; HL, Hydrolysis lignin; KL, Kraft lignin; LiP, Lignin peroxidases; LiOH, Lithium hydroxide; $Mn(NO_3)_2$, Manganese nitrate; MnP, Manganese-dependent peroxidases; w.t.%, Mass fraction; MA, Muconic acid; NAD+, Nicotinamide adenine dinucleotide; OL, Organosolv lignin; PCB, Polychlorinated biphenyls; PHAs, Polyhydroxyalkanoates; KOH, Potassium hydroxide; PAHs, Polycyclic aromatic hydrocarbons; *P. putida*, *Pseudomonas putida*; p-TsOH, P-toluene sulphuric acid; *R. jostii*, *Rhodococcus jostii*; SiO2, Silicon dioxide; NaHS, Sodium hydrosulphide; NaOH, Sodium hydroxide; THF, Tetrahydrofuran; TCA cycle, Tricarboxylic acid cycle; UV, Ultraviolet; *vdh*, Vanillin dehydrogenase; VA, Veratryl alcohol; VP, Versatile peroxidase

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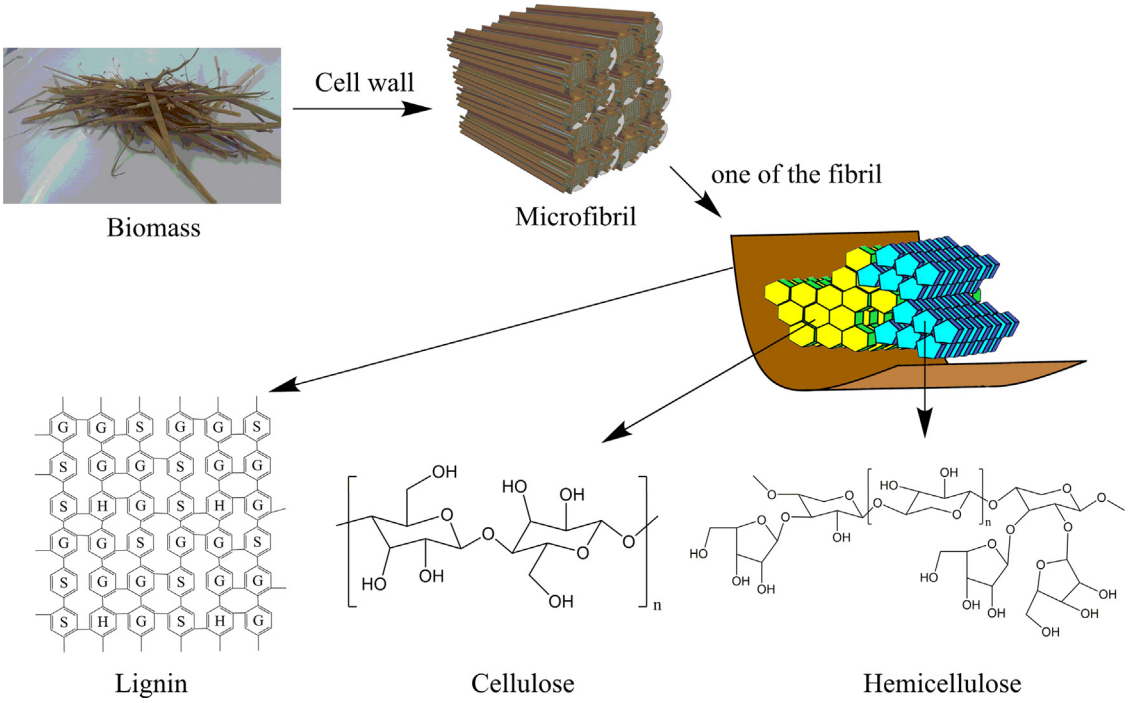

Fig. 1. Lignocellulose in biomass and its composition.

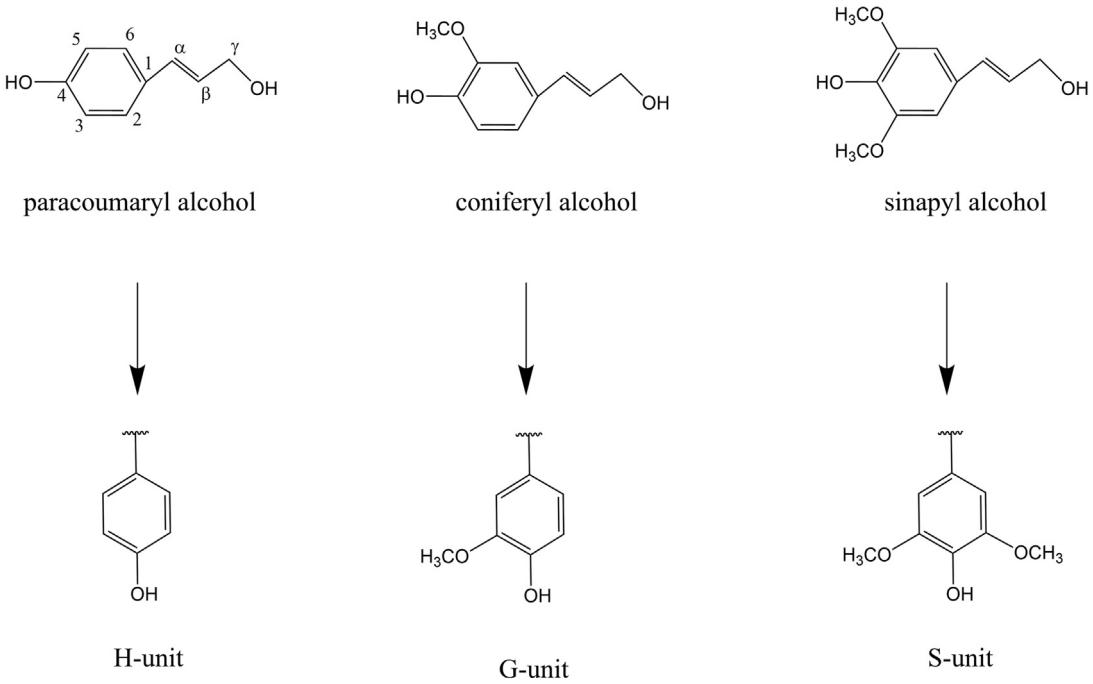

Fig. 2. The precursors and basic-unit in lignin molecule.

monomer alcohols [5,6]. There are two major linkages between these monomers: carbon-carbon linkages, also known as condensed linkages, and ether linkages (Fig. 3). The dominated linkage in the lignin polymer is ether linkages representing 56% or more in total linkages [7]. Due to the different ratios of these monomers in different sources of lignin, the exact ratios of linkages are also different in various species, like the most common ether linkages, β-aryl ether (β-O-4), represents around 50% and 60% of total linkages in softwood and hardwood, respectively [8]. Aryl ether linkage is easier to be cleaved when compared to condensed linkages during the lignin depolymerization and conversion [9], thus the cleavage of the β-O-4 is also considered as a critical step of lignin depolymerization for utilizing lignin as raw materials to produce other chemicals [10]. In this review, we focus on introducing different aspects of depolymerization methods and using these techniques to produce lignin-derived materials.

Using technical lignin for different industrial applications has been studied for decades. The most common industrial application for kraft lignin is using it as fuel for heat generation. There are numerous studies investigating the potential application of lignin (Table 1) [11,12]. Furthermore, lignin also can be used as a sole carbon source for bacteria

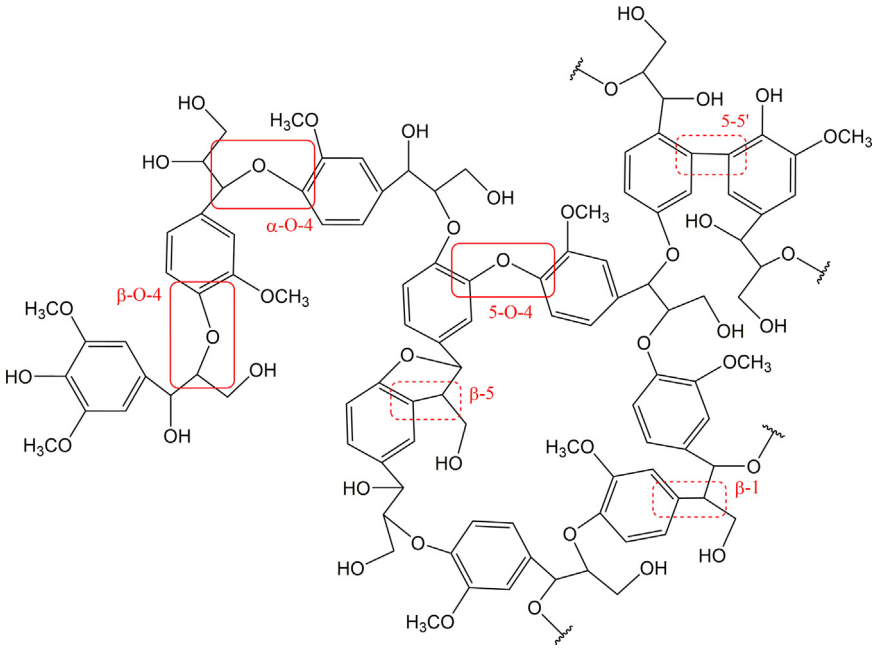

Fig. 3. Several typical linkages within the lignin molecule. The linkages marked by solid squares are ether linkages. The linkages marked by dot squares are condensed linkages.

culture [13] and produce triglyceride lipids during bacterial metabolism [14].

2. Lignin sources

Lignin can be classified as native lignin and technical lignin. Native lignin is referred to the original lignin structure in the lignocellulose without any modification. As a natural polymer, native lignin doesn't exist solely in nature. It always exists as part of the lignocellulose. Thus, most of the lignin being studied is modified lignin or technical lignin, which is the lignin extracted from biomass or recovered from the industrial by-product. Numerous studies are focusing on converting technical lignin to other value-add chemicals or products. The major source of technical lignin from industries is kraft lignin (KL) and there are several other types of lignin sources like hydrolysis lignin (HL), organosolv lignin (OL), pyrolytic lignin (PL), etc. The composition and molecular weight of these technical lignins are different according to their sources and extraction methods.

The technical lignin from the industrial by-product can be directly used as raw materials for other chemicals production. Aliphatic and aromatic hydroxyl groups are major constituents and active sites in technical lignin thus it also can be directly used as polyols for producing the polyurethane and replace 30% of petroleum-based polyols during the polyurethane production [21]. However, the reactivity of the technical lignin is much lower than the lignin fragment due to the reactive site is blocked by the complex structure. Compared to the technical lignin, the depolymerized lignin fragment can replace up to 50% of the petroleum-based polyols during the polyurethane production [22]. Therefore, the depolymerization can enhance the availability of the lignin and expose more reactive sites which favor to further utilization [23].

2.1. Kraft lignin

The kraft process is one of the major traditional methods for pulping and paper production. It represents almost 80% of the chemical pulp production [24]. During the kraft process, the wood is treated with the solution of sodium hydroxide (NaOH) and sodium hydrosulphide (NaHS) under a temperature range of 150–170 °C. After several hours of treatment, the ether bonds in the lignin structure can be cleaved and converted to small lignin fragments which are also known as alkali-soluble lignin. Almost 90% of lignin of wood could become soluble during the delignification and the liquid mixture is named as black liquor [25]. Kraft lignin can be recovered by adding acid to acidify the black liquor to pH 5.0 or lower and it can be precipitated during the acidification. The advantage of using acidification to produce kraft lignin is that the Na^+ and S^{2-} in the solution mixture can be regenerated and reused in the kraft process [26,27]. This process has been already applied to the industrial production and introduced into the market. In 2013, 27, 000 t of kraft lignin were produced [28]. However, the current major application of the kraft lignin is used as fuel for energy production. The major reason for using it as fuel is related to its

Table 1
Potential application of lignin in various fields.

Applications	Descriptions
Energy production [15]	Lignin can be generated during the kraft process which also can be used as fuel for heat generation. Gasification of lignin also can produce syngas for energy production.
Dispersant [16]	Enhancing the dispersion of various insoluble particles like synthetic dye.
Biodegradable polymer [17]	Powdered lignin can be added during the polymer production and enhance the polymer biodegradability
Protective UV-absorbents [18]	Adding lignin to line fabrics can improve the UV barrier properties.
Nanoparticles [19]	By precipitating lignin in solution, a non-toxic and environmentally friendly nanoparticle can be produced. It can be further used in drug delivery and heavy metal absorption in the environment.
Phenolic resins [20]	Organosolv lignin can be directly replaced phenol which is used for phenol-formaldehyde resins production and it shows great curing properties compared to lignin free resins.

chemical properties. Kraft lignin is hydrophobic and it is not an active chemical compound unless it is modified to improve its reactivity. Kraft lignin also contains the aliphatic thiol groups which cause KL has a special odor [25,29].

2.2. Organosolv lignin

Lignin in the biomass can be dissolved in the organic solvent under certain condition and the lignin recovered from liquid fraction is named as organosolv lignin. Comparing to other lignin extraction methods, the organosolv process shows the ability to produce high-purity lignin from biomass, it also able to remain most of the cellulose residue for bioethanol production [30]. Therefore, the organosolv process is also considered as one of the promising methods for biomass utilization and organosolv lignin has become one of the famous technical lignin in the biorefinery. Previous studies have investigated various organic solvent including alcohol, acetic acid, ketone and ester [30–32] for dissolving different sources of lignin, including corn, wheat, pine wood, aspen trees and bamboo [33–37]. Organosolv lignin is also considered as one of the ideal lignin for biomaterial production due to its high purity, sulphuric-free and less modification which favor to the downstream process during the production [38].

2.3. Hydrolysis lignin

One of the promising applications of lignocellulose is ethanol production. Cellulose in the lignocellulose can be fermented to bioethanol with the help of various enzymes. However, the lignin in the lignocellulose forms a complex “shield” which blocks the interaction between enzyme and cellulose which lowers the yield of bioethanol production. The lignin which can’t react with the enzyme is left as residue and become hydrolysis lignin [39]. The hydrolysis lignin contains 50–75% of lignin and other components like carbohydrate, mostly the untreated cellulose and oligosaccharides, nitrogen, etc. Comparing to kraft lignin, hydrolysis lignin is sulfur-free, has a low phenolic ratio and its structure is similar to the native lignin.

The potential applications of hydrolysis lignin include producing sorbents, resins, etc. [40,41]. Furthermore, the hydrolysis lignin has a higher reactivity than the kraft lignin due to its higher content of hydroxyl groups. It suggests that the hydrolysis lignin have a high potential for producing other polymeric chemicals [42,43]. However, its high impurity and low solubility restrict its applications [42]. Extensive studies had been focusing on using hydrolysis lignin but various studies indicated that the hydrolysis lignin needs multiple steps of modification and purification before applying to other usages [41], thus the major application of hydrolysis lignin is similar to kraft lignin, burnt as fuel and generating heat for energy production [44]. However, due to the numerous studies focus on using lignocellulose for biofuel production, using hydrolysis lignin for industrial applications can be a platform or direction in the future.

2.4. Pyrolytic lignin

Fast pyrolysis is one of the common methods for lignin conversion and depolymerization. After the pyrolysis, lignin or lignocellulose could be converted into a highly viscous bio-oil. A water-insoluble fraction can be obtained by adding water to the bio-oil and these water-insoluble solid are commonly known as pyrolytic lignin (PL). PL can be further purified by solubilizing in an organic solvent and removing the ash and other inorganic compounds. Unlike other technical lignin, PL is produced by the repolymerization of lignin oligomers during the pyrolysis. Various studies show that the polydispersity index of the switchgrass pyrolytic lignin (2.22–2.92) is significantly lower than the organosolv switchgrass lignin (4.3) which indicated that the pyrolytic lignin may be more uniform in particles mass [45,46].

There are various aspects of the potential applications of the pyrolytic lignin. The study from Fortin et al. and Mullen et al. indicated that the non-purified pyrolytic lignin can provide more heating value during the combustion [46,47]. Except using for heat generation, pyrolytic lignin also can be used as raw material for value-added chemicals production. Gayubo et al. have proposed a strategy for separating pyrolytic lignin from cured bio-oil by co-feeding methanol. These processes are able to prevent the catalysts deactivation caused by the PL deposition and isolated the PL for further valorization [48]. Wang et al. supposed a cost-effective method for converting pyrolytic lignin to high purity value-added chemical hexamethylbenzene with the presence of the γ-Al_2O_3 under atmospheric pressure of N_2 [49]. Beside chemical production, pyrolytic lignin can be directly used as a starting material for producing carbon fiber with advance properties [50].

3. Thermochemical methods for lignin treatment

Increasing temperature is a common and effective treatment for destroying chemical bonds, thus the thermochemical and other physical treatments have attracted numerous researcher's attention. Thermochemical treatments include pyrolysis, hydrogenolysis, hydrolysis, etc. These treatments represent the thermal treatment of the lignin with or without other catalysts. The physical treatments are not only referring to mechanic treatment, but also include using other equipment-assistance for improving the depolymerization efficiency, like treatments with ultra-sonication and microwave, and these treatments usually have to involve other catalysts for completing the depolymerization.

3.1. Pyrolysis

Pyrolysis is one of the most widely studied methods for lignin or biomass depolymerization and conversion. Pyrolysis is a thermal treatment of organic substance without or under a limited amount of oxygen. Due to the absence of oxygen, the lignin is degraded but doesn’t further convert to carbon dioxide. Most of the final products obtained from pyrolysis of lignin are liquids or gases. These products contain massive amounts of various aromatic monomer and they show a great potential that pyrolysis can be an effective method for converting lignin and biomass to other biomaterials [51]. In general, increasing the severity of the reaction condition can lower the molecular weight of the depolymerized lignin fragments [52]. Except for the severity of the reaction condition, the efficiency and the depolymerized products can be modified through several factors, including the source of lignin [53], solvent, catalysts [54], reaction time [55]. During the pyrolysis, lignin can be gasified and produce several gases at high temperature. These gases include hydrogen, carbon dioxide, carbon monoxide, and methane. The carbon monoxide and hydrogen mixed in the gases can be further processed to produce syngas for other applications [56,57].

Lignin depolymerization through pyrolysis usually starts with the cleavage of weak linkage at low temperature and further break down the strong linkages at higher than 450 °C. The depolymerized lignin fragments from the beginning stage are further converted to other chemicals at high temperature, including benzene ring cracking and gases release [58]. Pyrolysis can be performed in multiple ways but most of the pyrolysis process can be divided into two different stages: the first stage of pyrolysis and the secondary stage of pyrolysis [59].

The first stage of pyrolysis happens when the pyrolysis reaction temperature is within the range of 150–400 °C. Most of the ether linkages are destroyed including β-O-4 (Fig. 4) which is one of the most abundant linkages within the lignin molecule. The model chemical studies also indicated that the non-phenolic ether bonds are easier to be cleaved than the phenolic ether bonds and the condensed linkages like β-1 and biphenyl bonds also can be cleaved in this stage, even though it is not very effective [60]. Softwood lignin usually contains a greater number of condensed linkages than the hardwood lignin, thus softwood lignin usually lefts higher amount of residue than hardwood lignin

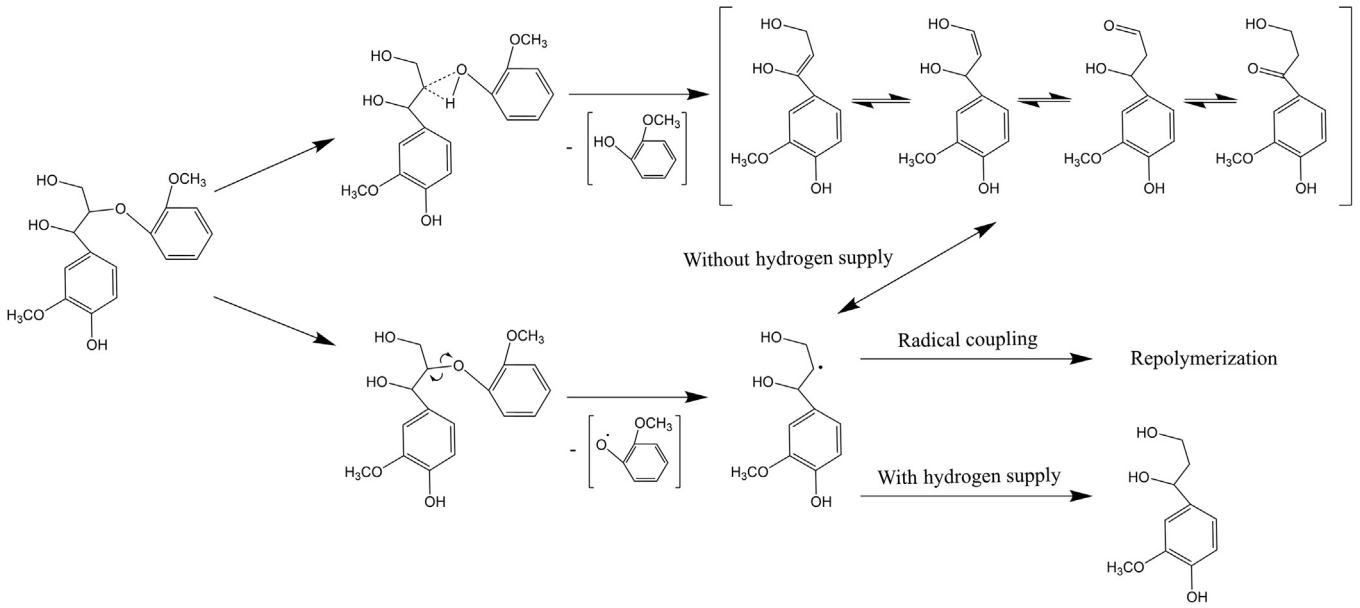

Fig. 4. The purpose mechanism of cleaving the β-O-4 linkages by pyrolysis.

[53]. During the first stage pyrolysis, the aromatic methylated groups and the condensed linkage are stable, therefore the depolymerized lignin fragments from first stage pyrolysis usually are the basic unit of lignin, like 4-methylguaiacol, syringol, coniferyl alcohol, and some lignin-derived chemicals like vanillin, isoeugenol or some unsaturated alkyl [61,62]. Under pyrolysis environment and without the hydrogen supply from the hydrogen donors, the amount of hydrogen is not enough for the depolymerized lignin fragments and other intermediates to form a stable chemical molecule, therefore these intermediates undergo the repolymerization and form the dimers or oligomers. Furthermore, the repolymerization process is trending to form the condensed bonds instead of ether bonds. Thus, the repolymerized products are more resistant to the depolymerization and increase the difficulty of further conversion. However, when the temperature reaches as 350 °C or higher, the hydrogen radicals released from lignin molecule can be sufficient for stabilizing the intermediates or depolymerized fragments, thus the yield of lignin-derived monomers could be increased [63–65].

The second stage of pyrolysis is the pyrolysis temperature higher than 400 °C and usually is up to 800 °C. Unlike the first stage pyrolysis, most of the linkages are broken down and the severer gasification starts during this stage. At 450 °C, the substituent methoxyl groups are cleaved and hydroxyl or methylated groups bonded to the aromatic units [66]. Therefore, the major products from first stage pyrolysis like syringols are further converted into *o*-vanillin, guaiacol and *o*-quinone methide [65]. When the pyrolysis temperature further increases to 550 °C, the benzene rings are broken down and converted into non-condensable gases [67]. The second stage pyrolysis product catechol can be degraded into carbon monoxide and cyclopentadienone which can be further decomposed into carbon monoxide and acetylene. Other products from second stage pyrolysis like pyrogallol can be converted to large amounts of carbon dioxide and carbon monoxide [68]. However, the formation of coke and polycyclic aromatic hydrocarbons (PAHs) lower the yields of the monomer and remain remarkable carbon content in the residue. The first stage of coke formation happens at 450 °C. Hosoya et al. indicated that the methoxyl group from guaiacol is responsible for the significant amount of coke formation [69]. The second stage of coke formation happened when the temperature is higher than 550 °C and various products are involved in the coke formation, including catechols, pyrogallols, and cresols. Previous studies also indicated that the increase of the methyl group in the depolymerized products could increase the yields of the coke formation [68]. Thus, the methoxyl and methyl groups are one of the major reasons for the coke formation during the second pyrolysis. Moreover, due to the high percentage of methoxyl group presented in the syringol, syringol has a higher chance to form the coke during the pyrolysis and Asmadi et al. also shows that the yields of monomers from syringol are lower than the guaiacol [65]. However, Patwardhan et al. indicated that by increasing the pyrolysis temperature from 300 °C to 700 °C, 60% of the char formation could be suppressed and the yields of monomers including phenol, 2-methyl phenol, 2, 5- dimethyl phenol could be increased., especially with a high heating rate [3,55]. Windt et al. also suggested that low temperature and long reaction time increase the severity of the repolymerization [70]. Therefore, fast pyrolysis recently has attracted various attentions which can be considered as a better method for lignin thermochemical conversion.

Except for the usual pyrolysis, nowadays pyrolysis is commonly combined with various catalysts and solvents for improving its performance. Due to the closed environment during the pyrolysis, the addition of catalysts or solvents can offer several useful accompanying molecules like hydrogen donor or oxidant to improve the efficiency of pyrolysis by assisting demethoxylation or demethylation and providing sufficient hydrogen or hydroxyl group for preventing repolymerization and condensation. One of the well-known catalysts is zeolite. Most of the studies indicated that zeolite ZSM-5 with a wide range of Si/Al ratio can improve the efficiency of the depolymerization and increase the yields of aromatic monomers [61]. Furthermore, such zeolites can change the depolymerized lignin molecule dramatically by effectively converting lignin-derived phenolic compounds to aromatic hydrocarbons [71–73]. However, previous studies also indicated that the nature of pore on the zeolite causes the repolymerization and coke formation. Lignin which contains a high amount of simple phenols also causes the zeolites to deactivate quickly [61,74]. Some metal oxides also have been investigated as catalysts. Ma et al. show that cobalt can enhance the yields of various monomers and depends on the supporting materials like the ZSM-5 supported cobalt can convert lignin to aromatic hydrocarbons effectively. Furthermore, copper and nickel also can convert lignin to the specific phenolic product with high selectivity [75].

Pyrolysis can be an effective method for converting and liquefying lignin to bio-oil for other applications. However, the low-selectivity reaction limited its application in specific chemicals production. Furthermore, the severe reaction condition and short reaction time also

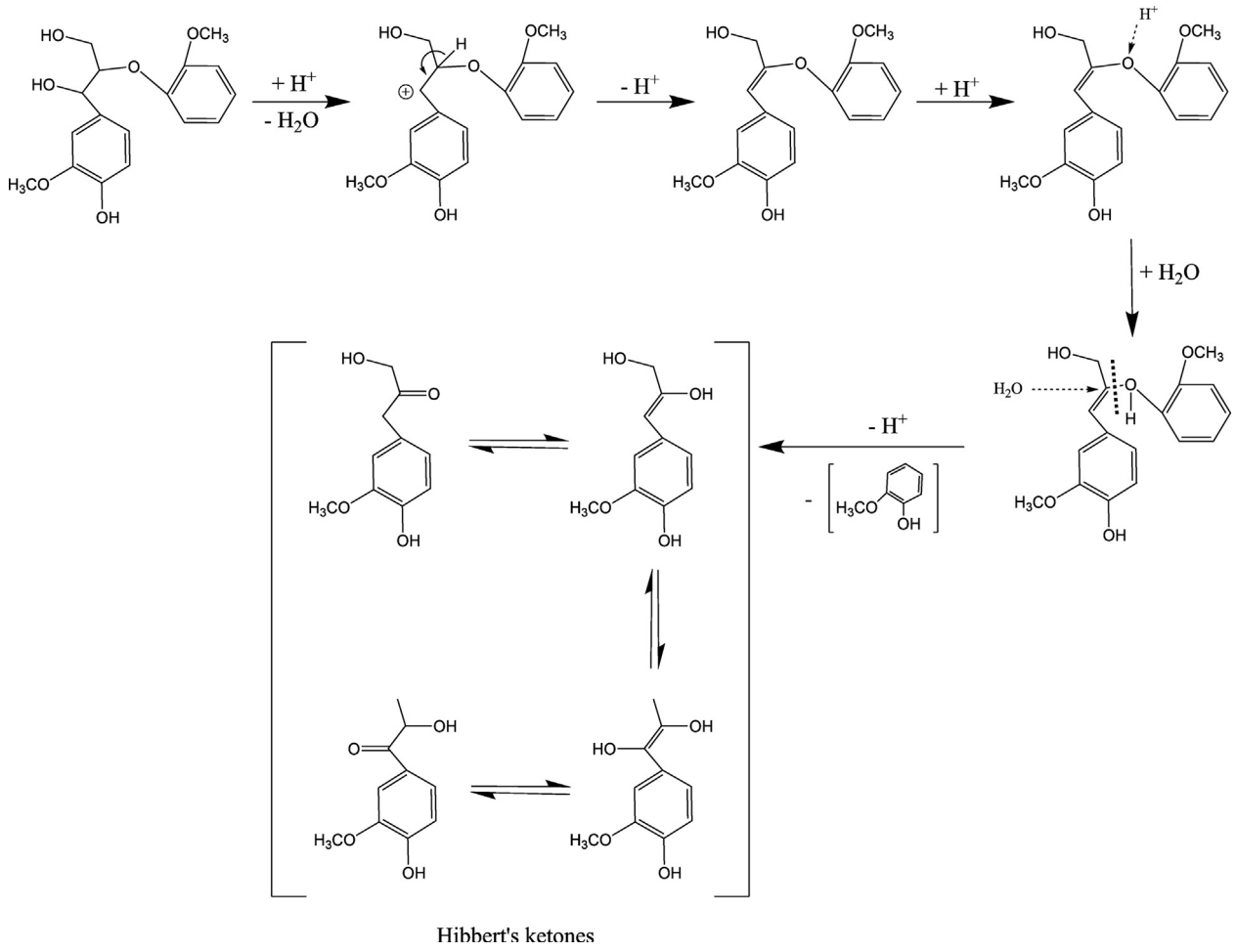

Fig. 5. The purpose mechanism of cleaving the β-O-4 linkages with acid-catalysts Adapted from [93].

cause the difficulty in product separation and restricted the studies on the mechanism of pyrolysis or catalyst-assisted pyrolysis which is favourable to valuable chemical production.

3.2. Microwave assisted depolymerization

The use of the microwave to assist the lignin or biomass conversion has been studied for decades [76,77]. Microwave can be an alternative method for heating instead of the traditional bath heating and it has been widely applied in the lignin and biomass thermochemical conversion [78]. Microwave can apply high energy of electromagnetic radiation into the lignin and biomass molecule. These radiations can cause the rotation of the polar molecules and ionic conduction, then further generating a massive amount of heat [79]. Therefore, compared with the traditional heating, microwave can prevent the physical contact between the heating source and material which can avoid the surface overheating and reduce the reaction time [77,80]. Moreover, the microwave is also proposed as an economic method for biomass heating and pyrolysis [81,82]. Liew et al. show that microwave pyrolysis could be an economic approach for converting biomass to valuable and high-quality active carbon [82] Furthermore, microwave contains lesser mechanic unit and can be accurately controlled during the operation [83].

Previous studies indicated that the use of microwave can improve the reaction selectivity with metal salt as catalyst. Zhu et al. use ferric sulfide as the catalyst and it further compares the performance of the microwave-assisted depolymerization to the traditional heating. The results indicated that the use of microwave can specifically cleave the condense linkages Cα-Cβ under 160 °C and it can enhance the ratio of soluble fraction from 67% to 86% [84].

Even though microwave is usually used as a heating method for lignin pretreatment or depolymerization with other catalysts, microwave also can be used as a heater for pyrolysis or pretreatment before pyrolysis. Using the microwave for pretreatment can cleave the weak linkage such as ether bond and remove the methoxyl group. Therefore, the char formation during the pyrolysis can be suppressed. Moreover, Duan et al. indicated that the microwave-assisted pyrolysis of alkali lignin can increase the yields of phenolic compounds like catechol, 2-methyl phenol from 3.81% to 14.15% and decreases the yields of guaiacols like creosol, eugenol from 36.56% to 22.36% at 200 °C, 60 min [85].

Except using for depolymerizing lignin, microwave also can be assisting liquefaction or solubilization of lignin by accelerating the heating rate. Due to the high heating rate, lignin can be easily dissolved in ionic liquid at a lower temperature and a shorter treatment period when compared to conventional heating methods [86]. During the heating, the electromagnetic field may also affect the chemical transformation and cause special thermal effects which are not able to be achieved by the traditional heating [87]. Furthermore, the biopolyols converted by microwave can be directly applied into the downstream process for polyurethane foam production [88,89] and these results show that the use of microwave for lignin liquefaction and biopolyols production has a great potential for industrial application.

4. Chemical or catalyst for lignin treatments

Based on the work of Wang et al., the chemical catalysts used for lignin depolymerization generally can be further divided into five different categories, including: (1) acid-catalyzed, (2) base-catalyzed, (3) metallic catalyzed, (4) ionic liquids-assisted catalyzed and (5) supercritical fluids-assisted catalyzed [90]. Except for the above categories, hydrogen peroxide also is one of the common catalysts for lignin depolymerization. Different chemical catalysts can be combined at the same time or applied into a different stage of the depolymerization process for improving the efficiency and producing desired products. These catalysts have their own advantages and disadvantages. Compared to the thermal treatment, the reaction condition is milder and the catalysis has a higher selectivity. However, environmental damages are also a major concern of using chemical catalysts.

4.1. Acid catalysts

Acid has been used as a catalyst for lignin depolymerization since 1943. The purposed mechanism of acid-catalysis of β-O-4 linkages is shown in Fig. 5. Hewson et al. indicate that combining ethanol and hydrochloric acid can depolymerize lignin and convert into several small molecules [91]. Except for using hydrochloric acid, other common acids also have been investigated. The diluted sulphuric acid also can carry out the depolymerization process while mixing with ethanol or water as a solvent [92]. The depolymerization process can be achieved under 2 MPa pressure and 250 °C for 1 h. The results show that using sulphuric acid as catalyst and 1:1 water-ethanol mixture as the solvent can produce 70 wt% depolymerized lignin. The depolymerized products are examined by H NMR and the result shows that the total hydroxyl number is around 442.0 mg KOH/g. Furthermore, around 87 wt% of carbon can be recovered from the lignin [24,92]. These results indicate that depolymerized lignin can be a suitable raw material for resins or foams production because these depolymerized products still remain a high amount of hydroxyl and carbon content.

Recently, p-toluene sulphuric acid (p-TsOH) is used as a hydrotrope to dissolve the lignocellulose in the purpose of delignification [94]. During the delignification, some of the depolymerized products can be produced. Even though the depolymerization is not effective, unlike other strong acid catalysts, it doesn't require harsh reaction condition. It can dissolve the lignin at 80 °C within 20 min. It provides a potential platform for low-cost acid-catalyzed depolymerization.

Even though the acid-catalyzed depolymerization is widely studied, there are several disadvantages which have to be overcome. It is widely reported that the depolymerization process requires relatively severe reaction condition like high temperature, high pressure, long reaction time and involve the use of corrosive chemicals. The wastes from the depolymerization process are also considered as environmental pollutants. Furthermore, repolymerization is always observed during the acid-catalyzed depolymerization [95]. The intermediates or depolymerized products could be condensed together and form macromolecules which could lower the yields of the desired products.

4.2. Base catalysts

Base catalyst also is a well-studied catalyst for lignin depolymerization. The purposed mechanism of base-catalysis of β-O-4 linkages is shown in Fig. 6. Thring et al. indicated that the use of sodium hydroxide can increase the yield of depolymerized lignin more than 4-folds when compared to the control which is without any alkaline [96]. Previous studies focused on using NaOH as the catalyst for lignin depolymerization due to the low cost and it was commonly used in industry. Yuan et al. indicated that with the presence of phenol, alkaline lignin can be almost completely degraded with 5% NaOH and only 1.4 wt% of solid is generated at 260 °C, 1 h [24,97]. Instead of using NaOH, multiple bases also have been studied, including KOH, CsOH, $Ca(OH)_2$, etc. Interesting, Evans et al. indicated that using the strong bases, like KOH, NaOH, can convert and produce more depolymerized products rather than the weak bases, like $Ca(OH)_2$, LiOH [98]. Furthermore, the strong base also can reduce the char formation and remain the reactivity of the phenolic compounds during the depolymerization [99,100].

However, Knill et al. indicated that using a low concentration of base catalyst cannot catalyze the lignin depolymerization in water, almost no depolymerized products can be observed [102]. Therefore, most of the studies are using organic solvents, like ethanol, polyethylene glycerol, isopropanol, instead of water [92,103–105]. However, these organic solvents also can form a condensed structure with the lignin molecule [106]. Furthermore, the carboxylic acids which are produced during the depolymerization could further lower the pH of the reaction mixture and result in the repolymerization [107]. Thus, the repolymerization is also observed during the base-catalyzed depolymerization and this could lower the depolymerization efficiently and increase the amount of the residual lignin.

4.3. Metallic catalysts

Using acid or base catalyst is mainly focusing on the cleavage of the ether bonds. However, these methods are difficult to produce specific products. Furthermore, base or acid catalyzed depolymerization usually requires relatively severe reaction conditions, like high temperature (250 °C to higher than 300 °C) and high pressure (from 5 to 10 MPa) [108–110]. These conditions cause the depolymerization process to become costly and difficult to handle, thus numerous studies are looking for methods or catalysts which can catalyze the depolymerization process under a mild condition with high selectivity and several metals have been selected as potential catalysts for further study.

One of the most widely studied metallic catalysts is nickel. The purposed mechanism of metallic-catalysis of β-O-4 linkages is shown in Fig. 7. Song et al. indicated that metallic nickel can be a potential metallic catalyst to produce phenolic chemicals. Nickel is able to specifically cleave the ether linkages. Furthermore, it is able to hydrolyze the carbon-hydroxyl linkage at the side chain to alkane specifically [111]. Song et al. indicated that Ni can convert more than 50% of birch wood lignin to propylguaiacol and propylsyringol with high selectivity, 25% and 72% respectively, in ethyl glycerol at 200 °C, 6 h [112]. Furthermore, these studies also indicated that nickel can catalyze the depolymerization process under a mild reaction temperature (lower than 200 °C). Moreover, nickel combined with other metal can form bimetallic alloy Ni-M (M can be Ru, Rh, Pd, Au, Fe, Mo, Ti) [113–119]. Using bimetallic catalyst can increase the reactivity and selectivity due to the synergistic effect [120,121] and previous studies also indicated that these reactions can be achieved under 120 °C with high selectivity [113–115]. However, there are several limitations of the using nickel-bimetallic catalyst. The noble metals used in the bimetallic alloy are expensive which could increase the cost of the depolymerization. The noble metallic catalysts also cause the over-hydrogenation on the aromatic compounds under several reaction conditions which decreases the yield of the phenolic products. Thus, many efforts have been performed to lower the cost, including the use of cheap metal to replace the noble metal for synthesizing a non-precious alloy and improve these catalysts reusability [112,118,122].

Except for Ni, many metallic catalysts also have been studied including noble metals (Ru, Pd, Pt, Ti), cheap metals (Cu, Mo, Al, Fe, Zn), their combination and alloy [118,123–126]. Ye et al. show the potential of Ru in specifically converting corn stalk lignin to 4-ethylphenol and 4-ethylguaiacol with the yields of 3.10 wt% and 1.37 wt% at 275 °C, 90 min, 2 MPa [127].

Even though the metallic catalyst can catalysis and convert lignin to specific chemicals with high selectivity, the use of noble metal, catalyst deactivation and low conversion rate (around 50–60%) could limit the application of metallic catalysts in lignin depolymerization due to the cost of the processing, especially when compared to other chemicals

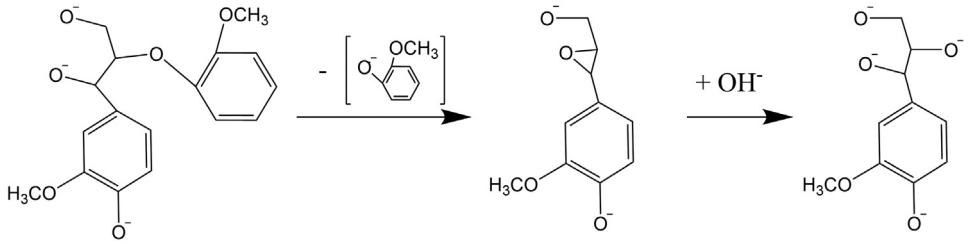

Fig. 6. The purpose mechanism of cleaving the β-O-4 linkages with base-catalysts Adapted from [101].

like acid, base which can almost completely convert lignin to other valuable chemicals during the reaction.

4.4. Ionic liquids assisted catalysis

The ionic liquid is widely defined as salts with a melting point less than 100 °C. Their unique physical and chemical properties have drawn remarkably attentions and these properties show the potential for industrial application including having a flexible characteristic which can be modified by changing the cation and anion in the salt, a low melting point and negligible vapor pressure which can convert salt to a high concentration ionic liquid easily and providing a strong environment for electrochemical reaction. Other properties like low volatility, inflammability, and high thermal stability also favor the industrial application [128].

The ionic liquid usually is used as a solvent and cooperates with other catalysts to depolymerize lignin due to that it is able to control the degree of the oxidation [129,130]. Several combinations of ionic liquid and metallic catalysts, including Cu, Mn, Co, have been studied. Stärk et al. reported that the combination of $Mn(NO_3)_2$ and 1-ethyl-3-methylimidazolium trifluoromethane sulfonate can selectively convert more than 63% of organosolv beech lignin to 2, 6-dimethoxy-1, 4-benzoquinone with the yield of 11.5 wt% at 100 °C, 24 h [131–133]. Interestingly, previous studies also indicated that the anion in the ionic liquid plays a critical role during the lignin depolymerization due to that it is able to stabilize the intermediates during the lignin depolymerization, thus it can significantly affect the yields of the monomeric products [132,134]. Furthermore, ionic liquid 1-octyl-3-methylimidazolium acetate has been studied as a catalyst for lignin depolymerization alone. It can convert more than 96% of lignin model molecules to phenolic compounds under mild reaction condition [130,135]. However, the high cost of the ionic liquid restricts its application and practice in the industrial operation. Furthermore, the ionic liquid usually has the interaction with the aromatic compound derived from lignin, thus it causes the difficulty of separating the ionic liquid from the monomeric products. This could become one of the major obstacles for its application and the study from Dier et al. has tried to increase the reusability of the ionic liquid [136].

4.5. Sub- or supercritical fluids assisted catalysis

When solvents under extremely high temperature and pressure, they become sub- or supercritical fluids and exhibit several different properties when compared to ambient condition. Supercritical fluids usually contain both liquid and gas properties. They have low viscosity and high diffusivity which allow the fluids permeate into the lignin molecule structure. Furthermore, water under supercritical condition exhibit a low dielectric constant which is similar to a non-polar organic solvent, thus water can solubilize several organic compounds effectively [137]. Saisu et al. show that with the presence of phenol, almost all of the organosolv lignin can be depolymerized and converted into 2-cresol with the yield of 7.15 wt% by supercritical water ar 400 °C, 1 h [138]. Similar researches had been conducted under different conditions, from 350 °C to 400 °C, and pressure, 25–40 MPa. The products from depolymerized lignin are further divided into methanol soluble and methanol insoluble. The soluble fraction mainly contains catechol, phenol and *o, m, p*-cresols. Previous studies also indicate that the repolymerization of low molecular weight molecule is observed in the supercritical condition [138–140]. Previous studies suggest that phenol can be added into lignin to inhibit the char formation and repolymerization [138,141,142]. The phenol can react with the decomposed fragment derived from lignin and block their active site for preventing the cross-linking reaction and repolymerization. The higher ratio of phenol to lignin shows a greater suppression [141,143]. However, the use of phenol for suppressing repolymerization is costly which would increase the expense in the overall process [144]. Except using supercritical water as the solvent, different supercritical organic solvents also have been applied in the depolymerization of lignin. Supercritical ethanol and methanol have been widely studied and performed in various conditions since the 1990s [98,145]. Cheng et al. reported that using supercritical ethanol for pine sawdust lignin depolymerization is more reactive and effective when compared to methanol. Only 12 wt% of

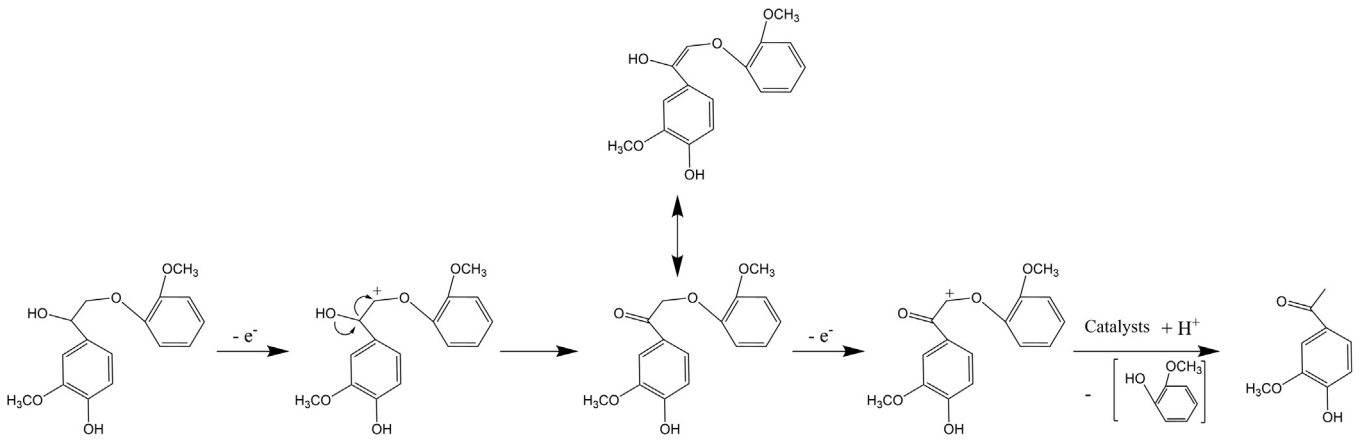

Fig. 7. The purpose mechanism of cleaving the β-O-4 linkages with the metallic catalyst.

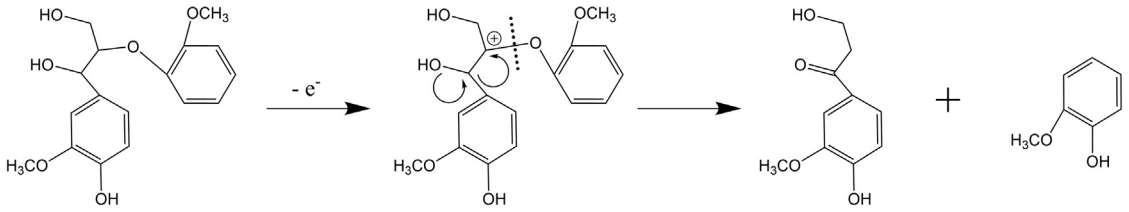

Fig. 8. The purpose mechanism of cleaving the β-O-4 linkages with the oxidant. The figure is showing one of the potential products. Actual products can be varied based on the oxidative degree.

solid is produced after the treatment at 300 °C, 20 min. Furthermore, 50% of ethanol or methanol can convert more than 95 wt% of pine sawdust lignin and produce 65 wt% of bio-oil which is 2-times higher than 100% ethanol or methanol [146].

Supercritical fluids can be an effective solvent for lignin depolymerization and solubilization. However, the high cost and severe reaction condition restricted its applications. Furthermore, the rapid hydrolysis of lignin in supercritical fluid enhance the difficulty of mechanism study and intermediate detection, thus the chemical conversion pathway need further study for improving selectivity and product separation.

4.6. Oxidative lignin depolymerization

Oxidation is one of the most common methods for lignin depolymerization and degradation [131,147,148]. The purposed mechanism of oxidation of β-O-4 linkages is shown in Fig. 8. Except for the chemicals in Sections 4.1 to 4.5, hydrogen peroxide and potassium permanganate are also widely used as oxidants for chemicals oxidation in industry or laboratory due to their high availability, low cost and easy to produce [148,149].

The use of hydrogen peroxide for lignin depolymerization or degradation has been well-studied for decades. Hydrogen peroxide usually combines with an appropriate catalyst like metallic catalysts or acid for selective lignin oxidation [150–152]. Hasegawa et al. used hydrogen peroxide to oxidize various type of lignin and their high performance liquid chromatography (HPLC) result shows that the alkali lignin can be depolymerized by 0.1% of diluted hydrogen peroxide and yield 45 wt% of to formic, acetic acid and succinic acid at 200 °C, 5 min. Similarly, the diluted hydrogen peroxide can also convert the organosolv lignin to 20 wt% of these three organic acids [153]. Jennings et al. also indicated that hydrogen peroxide has the ability to oxidize β-O-4 and β-1 linkage specifically. They also show that lower the reaction time and temperature may enhance the reaction selectivity [151].

However, the hydrogen peroxide also causes the over-oxidation which lead the aromatic or phenolic compounds ring-opened and became alkylic compounds [154,155]. Furthermore, the over-oxidation turns the product become unspecific and difficult to control. This could increase the complexity of the mixture and difficulty of separating the products [151,156].

5. Biological depolymerization

Various chemical catalysts and thermochemical treatments have shown great potential for highly efficient lignin depolymerization. However, both of them require relatively severe reaction conditions, including high temperature and pressure. Furthermore, these processes usually have some environmental risk factors which may cause damages to the environment and require a massive amount of energy for operation [157]. Therefore, the use of biocatalysts has been considered as an alternative method for lignin depolymerization. Biocatalyst usually is considered as an environmentally friendly catalyst because the enzymes or microbes involved in the biological treatments usually are from nature and they are not harmful to the environment. Furthermore, several enzymes can specifically catalyze the certain reaction, thus the use of biocatalyst can improve the reaction selectivity and suppress undesired side reaction such as repolymerization. Moreover, the biocatalyst required relatively milder reaction conditions when it compares to others, thus it lowers the requirement of the facility and reduces the formation of char. The biocatalysts use for lignin depolymerization and biomass treatment for various industrial applications like food, paper, and detergent have been studied for decades [158,159].

5.1. Organisms

Lignin is the most abundant phenolic polymer in nature and during a long time of evolution, numerous organisms have developed an effective metabolic system and methods to degrade and convert lignin to aromatic compounds and further convert these compounds to energy by multiple pathways [160].

5.1.1. Bacteria

Bacteria are considered as lesser effective than fungi in lignin degradation and one of the reasons is that there are fewer species in bacteria which are able to degrade lignin. However, several bacteria strains have been identified that it is suitable for lignin depolymerization and conversion. *Rhodococcus jostii* RHA1 is one of the well-studied lignin degraders and it has a great performance in consuming lignin to other compounds with the assistance of various enzyme [161]. Sainsbury et al. suggest that *R. jostii* RHA1 can cleave the β-O-4 with the help of dye-decolorizing peroxidase (DyP) and result in producing vanillin as the product [162]. Furthermore, Seto et al. also indicated that *R. jostii* RHA1 can degrade polychlorinated biphenyl and the further genomic studies also show that *R. jostii* RHA1 contains gene *benABCD* which can translate to various enzymes like 2-hydro-1,2-dihydroxybenzoate dehydrogenase for cleaving the linkage between biphenyl [163,164]. Therefore, *R. jostii* RHA1 also shows great potential for cleaving one of the common condensed linkage 5–5′ within the lignin molecule. Moreover, Sainsbury et al. also knock out the vanillin dehydrogenase from *R. jostii* RHA1 and the mutated *R. jostii* RHA1 can accumulate a certain level of vanillin in the cell. Salvachua et al. also indicated that *R. jostii* RHA1 is a robust bacteria for genetic engineering because the mutated bacteria can grow under high cell density environment with limited nutrients and have the ability to tolerate toxic metabolites [165,166].

Except for *R. jostii* RHA1, *Pseudomonas putida* KT2440 is also known as an excellent lignin degrading bacterium [166]. Previous studies indicated that *P. putida* can be a good candidate for degrading lignin to low molecular-weight molecule, then produce and accumulate polyhydroxyalkanoates (PHAs), one of the potential raw materials for bioplastic production, by converting lignin-derived aromatic compounds from lignin-rich medium [166–168]. Further genetic studies are conducted including domestication and pathway engineering. Martinez-Garcia et al. have eliminated 300 genes in the *P. putida* KT2440 genome and the engineered strain have significant improvement in almost all of the physiological status, including reducing the lag-phase, increasing the biomass yields, growth rate and tolerance to oxidative stress

[169,170]. Further pathway studies indicated that mutated *P. putida* can accumulate PHAs as metabolic intermediates by using several aromatic compounds as raw materials. However, using lignin as the carbon source for *P. putida* culture has not been tested yet [171]. Except for PHAs, pyruvate and *cis, cis* muconic acid (MA), which have the great potential for various bioplastic production, are able to be converted from lignin-derived aromatic compounds by introducing additional enzymes. These products can be further accumulated in the cell by blocking the specific metabolic pathway [172,173].

Amycolatopsis sp. is widely studied due to its effective depolymerization ability and high conversion rate of high molecular weight lignin when it compares to other bacteria [166]. Due to the well-understanding of several aromatic metabolism pathways in *Amycolatopsis* sp. [174,175], several metabolic engineering studies have been completed recently. Similar to *R. jostii* RHA1, Fleige et al. identified and cloned the vanillin dehydrogenase (*vdh*) from *Amycolatopsis sp.* 39116 genome. After the verification, they successfully increased the yield of vanillin 2.3 times by knocking out the *vdh*. Due to the gene knock out, the bacterium is not able to use vanillin as sole carbon resource for energy production, thus vanillin produced from ferulic acid is accumulated in the cells (Fig. 9). However, the study also indicated that vanillin could enter an alternative pathway which could slowly oxidize vanillin to energy [176]. Except for vanillin, MA also is one of the valuable chemicals can be recovered from lignin depolymerization. Barton et al. used genetic engineered *Amycolatopsis sp.* 39116 to produce and accumulate MA from depolymerized lignin lysate. The gene *catB*, which is an essential enzyme for utilizing MA for further metabolism, is knocked out, thus the MA can't be further oxidized and accumulated in the cell. Even though the deletion affects the cell growth rate, the mutant can accumulate 3 times more MA than the wild-type [177].

Although various bacteria show their potential in lignin degradation and conversion, the conversion efficiency of bacteria is much lower than fungi, especially white- and brown-rot fungi. Ahmad et al. reported that the activities of the extracellular enzyme for lignin degradation in bacteria are significantly lower than the enzyme from fungi. Furthermore, Salvachúa et al. show that after 7 days incubation, *R. jostii* is only able to convert 20% of dark shaded bars lignin and 27% of it with the presence of glucose [166,178]. Moreover, genetic modification cannot be applied to all bacteria species due to the lack of related genetic information [179].

5.1.2. Fungi

The fungus is one of the most studied microbes for lignin depolymerization and degradation. White rot basidiomycetes have been extensively studied in various aspects. They show a higher conversion rate and depolymerization efficiency when it compares to bacteria [166]. Due to strong ability in degrading lignin, white rot fungi have been applied into various industrial applications, including removing phenolic compounds from pollutants, delignification of biomass and increasing the cellulose ratio and improving biomethane production [180–184].

White rot fungi are the most effective microbe for degrading the native lignin in the wood [185]. Its great ability for degrading lignin may strongly relate to that white rot fungi can produce various extracellular oxidases including lignin manganese, laccases, and phenol oxidases [186]. The excessive amounts of these oxidases secretion also make the white rot fungi has an excellent performance in lignin degradation. *Phanerochaete chrysosporium* shows very high efficiency in removing lignin from biomass or waste, up to 99% [8,187]. Baltierra-Trejo et al. indicated that the strain *Pleurotus ostreatus* can effectively depolymerize lignin and produce several useful compounds like ferulic acid, syringyl alcohol [188]. Some fungi are able to depolymerize lignin and use the low molecular weight lignin or monomers as the carbon source for lipid synthesis. *Aspergillus fumigatus* is used for the fermentation of the wheat straw lignin-rich fraction and after the fermentation, various valuable chemicals are detected including syringic acid and vanillic acid, several short-chain fatty acids, including acetic acid and butyric acid are also detected [189]. However, Xie et al. cannot demonstrate that the fatty acid is mainly converted from lignin or another carbon source. A similar result has been presented by using a unique strain *Cunninghamella echinulata* FR3 which can effectively accumulate lipid by degrading lignocellulose. Moreover, Fenseca et al. also indicated that *C. echinulata* FR3 can degrade lignin with higher efficiency than cellulose or hemicellulose [190].

There are several genetic, proteomic and pathway studies focusing on improving the fungi performance and our understanding of how fungi depolymerize lignin. A laccase-encoding gene *lac I* has been isolated and identified from *Phlebia brevispora*. This gene is further cloned and transformed into *Pichia pastoris* for protein expression. The expression study indicated that lac I enzyme shows a high tolerance to various salt and solvents which shows its potential for using in various industrial applications [191]. Moreover, a novel laccase gene *lcc1* was isolated from *Ganoderma tsugae*. The knockout experiments show that *lcc 1* play an important role in lignin degradation. Furthermore, the depletion of *lcc 1* also has significant effects on the development of the mycelium and fruitbodies [192]. Proteomic studies indicated that

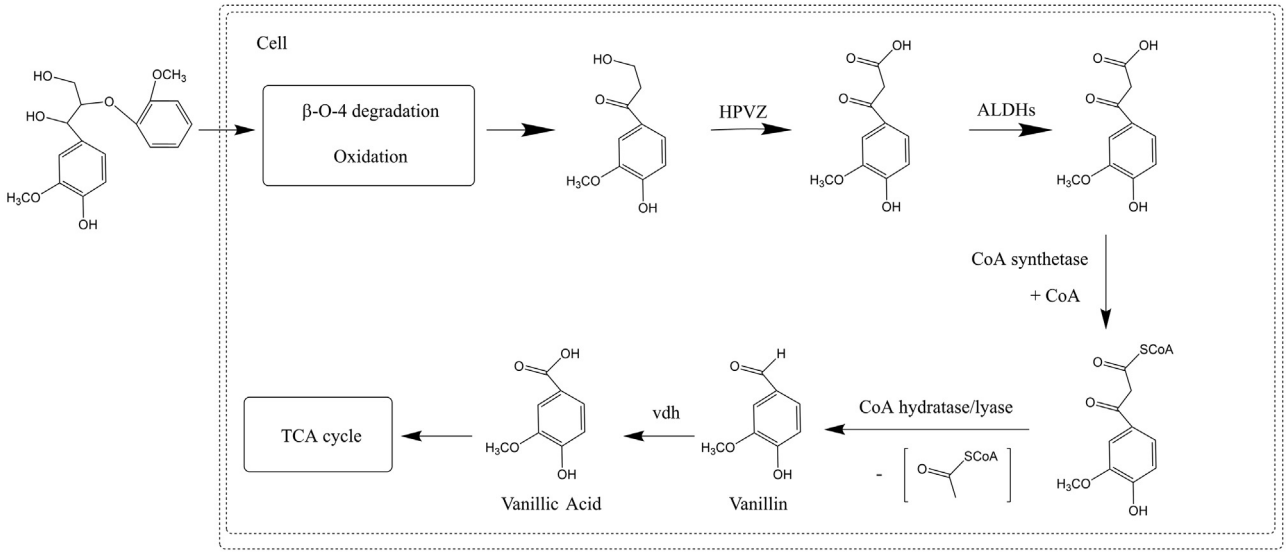

Fig. 9. The purpose pathway of converting lignin-derived compounds to energy.

manganese peroxidases and laccases are the most common lignin-degrading enzymes in basidiomycetes. Interestingly, several laccases show that they have the optimal reaction pH at 7 but usually these laccases also perform efficient and active in many different industrial environments [193]. Recently a novel β-etherase, which involved in the specific cleavage of β−O−4 linkage, is found in the *Dichomitus squalens*. Interestingly, a similar gene can be widely detected in various fungi or bacteria genomes but only a few of these species can exhibit the enzyme activity [194,195]. However, even though numerous genetic and pathway studies have been completed, unlike bacteria, a limited amount of studies are using metabolic engineering for improving valuable chemical production.

Extracellular laccase and various peroxidase are the major approaches for the fungi to degrade the lignin. However, even though fungi are more effective in lignin degradation when compared to bacteria due to the powerful extracellular enzyme, similar to other biological lignin depolymerization, the efficiency of the enzyme is much lower than chemical catalysis. Furthermore, the oxidoreductases produced by basidiomycetes also cause the lignin fragments repolymerization [196].

5.2. Enzymes

Enzymes which can effectively degrade lignin have been isolated from the fungi or bacteria and these enzymes have been applied in several *in vitro* experiments for lignin depolymerization or conversion study. Using *in vitro* enzymatic reaction can avoid several drawbacks including reducing the culturing time and the direct encounter between microbe and substrate [197]. Most of the *in vitro* experiments are conducted by using a single enzyme for cleaving lignin-model molecule as substrate. Other more complicated enzymatic digestion systems need a further understanding of molecular mechanism [198]. According to their reaction mechanism and environment, the enzyme for lignin degradation can be further classified as *in vitro* enzyme, mainly peroxidase and laccases, and *in vivo* enzyme.

5.2.1. In vitro enzymes

Most of the enzyme we found which can degrade lignin is non-specific cleavage. These enzymes mostly come from two enzyme families: peroxidase and laccase. Both of these enzymes catalyze the lignin by oxidation. Instead of catalyzing specific substrates or linkages, they attack the lignin molecule randomly. There are two groups of peroxidases have been well-studied, lignin peroxidases (LiP) and manganese-dependent peroxidases (MnP). Recently, versatile peroxidase (VP) and dye-decolorizing peroxidase (DyP) also attract various studied interest due to their versatile properties.

5.2.1.1. Laccases. Laccase is one of the common oxidases that can be isolated from various fungi and bacteria [199]. The most effective lignin-degrader white wood fungi also is one of the major laccase producers [193]. Laccase is a blue-copper phenoloxidase which can use oxygen as an electron acceptor and oxidize phenolic compounds (Fig. 10). The oxidized phenolic compounds could be converted into phenoxyl free radical which is an unstable intermediate and it could further lead to the polymer cleavage [200].

Even though the activity of laccase is limited to phenolic compounds, laccase also can cooperate with the mediator and degrade non-phenolic compounds [201]. The mediators are some small molecules which have the ability to transfer the electron, such as 2, 2'-azinobis (3 - ethylbenzothiazoline - 6-sulphonic acid) (ABTS) and 1-hydroxybenzotriazole (HBT). These accompany molecules can assist laccase to form a stable intermediate with the substrate [202]. With the help of the mediator, laccase can degrade almost 80–90% of lignin structure [203]. Numerous studies tried to increase our understanding of the laccase at the genetic level and improve its performance and stability. Laccase also can be applied in several treatments except for

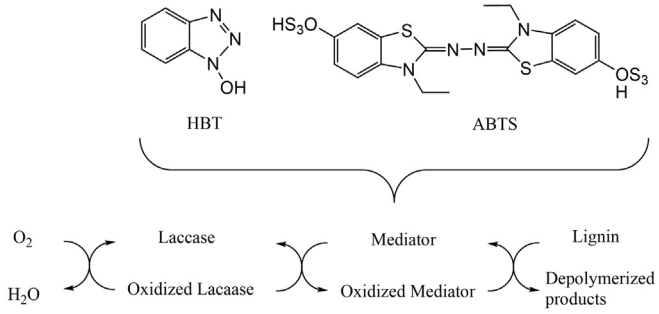

Fig. 10. The mechanism of laccase mediated lignin degradation.

depolymerization, including lignin-like chemical conversion, delignification [204–206]. Interesting, even though laccase plays an important role in lignin depolymerization, laccase is not an essential enzyme for microbes to depolymerize lignin. Previous studies indicated that even though with the limited amount or without the presence of laccase, the microbes are still able to degrade lignin [207,208].

5.2.1.2. Lignin peroxidases. Lignin peroxidase (LiP) also has been isolated from various fungi. LiP is a glycoprotein and it contains a heme group in its active center and it has a range of molecular weight from 38 to 43 kDa [186]. It requires hydrogen peroxide for initiating and catalyzing the non-phenolic compounds and phenolic compounds [209] (Fig. 11). It also required veratryl alcohol as an electron donor and cofactor to complete the catalytic cycle [210]. LiP also is known as the most effective peroxidase when compare to others peroxidases because it has a high redox potential which makes LiP able to oxidize various substrates which other peroxidases cannot oxidize [211]. Except using for lignin depolymerization, LiP is also used for delignification due to its great efficiency of removing lignin [212,213].

5.2.1.3. Manganese dependent peroxidases. Manganese dependent peroxidase (MnP) is an enzyme very similar to LiP. It is a glycosylated protein and needs hydrogen peroxide as an oxidant to initiate the catalytic cycle (Fig. 12). Afterward, MnP uses Mn^{2+} as reducing substrate and convert it into Mn^{3+}. The Mn^{3+} is a strong oxidant and it diffuses from the enzyme and starts to oxidize the lignin phenolic compounds. Therefore, the MnP can convert lignin phenolic compounds to phenoxy-radicals by Mn^{3+} and the phenoxy-radicals could cause the lignin depolymerization [214]. Similar to laccase, MnP plays an important role in the initial lignin depolymerization [215]. Furthermore, *in vitro* experiment indicated that the addition of MnP present in the system can enhance the effectiveness of the depolymerization process [216,217]. Usually, MnP only can oxidize phenolic compound, but MnP is also able to oxidize non-phenolic lignin model compounds with the presence of additional Mn^{2+}, previous studies also indicated that high level of Mn^{2+} can enhance the activity of MnP to degrade lignin in solid [218,219]. However, the repolymerization is also observed during the use of LiP and MnP for depolymerizing the synthetic lignin polymer [220,221].

5.2.1.4. Other peroxidases. Except for the enzymes mentioned in Sections 5.2.1.1 to 5.2.1.3, there are several peroxidases can be used for lignin depolymerization. Versatile peroxidase (VP) can be widely found in fungi *Bjerkandera* and *Pleurotus* and it has some similar catalytic properties with MnP and LiP [215,222]. VP is a bifunctionality enzyme. It can oxidize Mn^{2+} like MnP, it also able to oxidize various subtracts which have high or low redox potentials like LiP [223,224]. However, unlike MnP, VP can oxidize Mn^{2+} independently [225]. The protein crystal structural studies also explain the bifunctionality of VP [225–227] and due to its bifunctionality, VP has attracted several research interests. Except using VP for lignin depolymerization, VP also can be used for

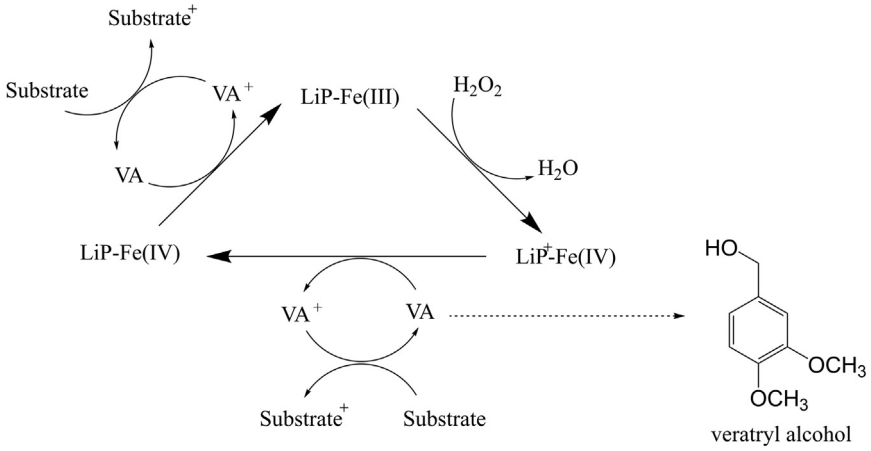

Fig. 11. The mechanism of LiP mediated lignin degradation.

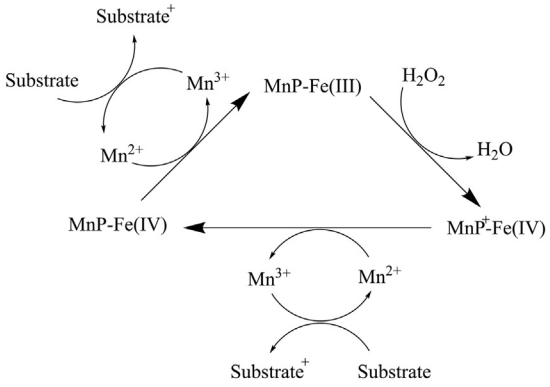

Fig. 12. The mechanism of MnP mediated lignin degradation.

delignification of biomass and decolorization of industrial waste [228,229]. The genetic studies related to VP also have been studied for a decade. The gene *mnp2* has been identified that it is responsible for encoding the VP and the inactivation of *mnp2* reduce the effectiveness of fungi in lignin degradation [230]. VP has been cloned and expressed in heterogeneous hosts, including *E. coli* and yeast, for the large-scale production and mutagenesis study [231–233].

Dye-decolorizing peroxidase (DyP) is another type of peroxidase which has been widely studied for lignin depolymerization. The first DyP was isolated from *Bjerkandera adusta* in 1999 [234]. The following studies also indicated that DyP unlike other peroxidases which are mainly found in fungi can be found widely in various bacteria [235,236]. Even though the sequence and structure of DyP are different from other peroxidases, they share similar catalytic properties and mechanism by using hydrogen peroxide and mediator for the substrate oxidation [237–239]. According to the sequence characteristics, DyPs can be classified into four classes [240]. Type A, B, and C can be widely found in the bacteria and type D are mostly produced by fungi [241]. Usually, type A and B DyP are produced by bacteria and they have a smaller size and lower activity. However, type C DyP is similar to type D DyP, both of type C and D DyP have a higher activity for substrate oxidation [242]. These four classes of DyP both have peroxidase activity and characteristic. However, even though Mn^{2+} is a necessary mediator for type B DyP oxidation, some type A DyPs doesn't have the Mn^{2+} oxidation activity and it may oxidize substrates by other routes [243,244]. Interesting, there is a novel DyP has been recently identified and it can oxidize the substrate with the oxygen in the air and without the presence of hydrogen peroxidase [245]. The mutagenesis study also has been conducted in DyP from *Pseudomonas putida* MET94 to improve the DyP performance in the industrial application by direct evolution [246].

5.2.2. *In vivo enzymes*

Many peroxidases have been studied as *in vitro* enzyme because they oxidize the lignin molecule outside the organism. As mentioned in Section 5.2.1, these laccases and peroxidases attack the lignin randomly, then convert the phenolic group to free-radicals and these radicals lead to the lignin depolymerization. After the lignin has been degraded to small molecules, the bacteria take up these monomers or oligomers and these small molecules undergo a series of conversion catalyzed by various *in vivo* enzyme. Most of the linkages within the lignin molecules have their specific metabolic pathways to cleave these specific linkages. The understanding of the enzymes involved in the pathway can develop an efficient and reliable approach with high selectivity for lignin depolymerization and conversion.

5.2.2.1. β-O-4 ether degradation. The β-O-4 ether bond is one of the major linkages within the lignin molecule and it almost represents 50% or more of the total linkages. Therefore, cleavage of β-O-4 ether bond is considered as an important step for lignin depolymerization [247]. The cleavage of the β-O-4 ether bond has been studied in various organisms, including *Sphingobium* sp. SYK-6, *Novosphingobium* sp. PP1Y, *Novosphingobium aromaticivorans* and *Dichomitus squalens* [195,248–250]. Both of them have similar pathway and mechanism (Fig. 13). β-O-4 degradation starts with LigD, a Cα-dehydrogenase. LigD oxidizes the hydroxyl group at Cα position, then the β-etherase,

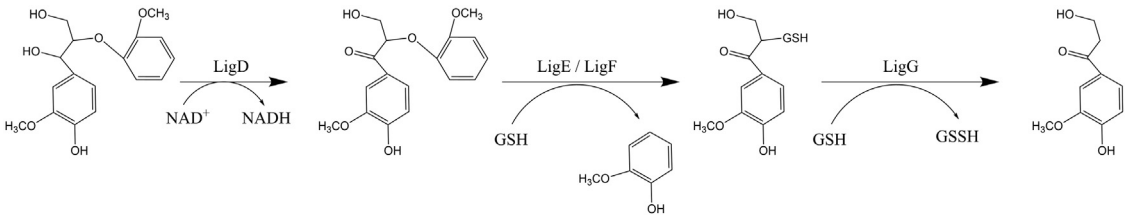

Fig. 13. The mechanism of LigDEFG mediated lignin β-O-4 model molecule degradation.

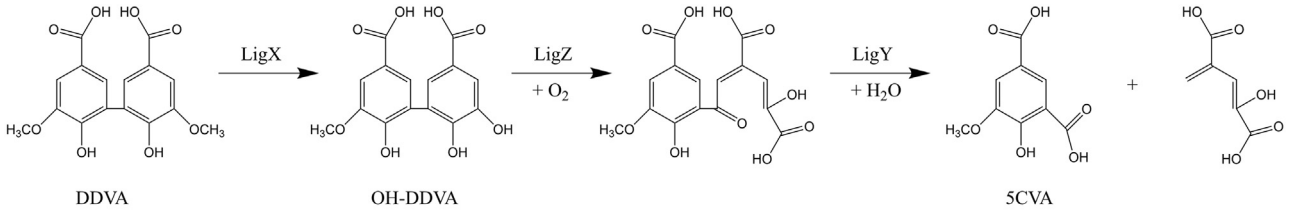

Fig. 14. The mechanism of LigXYZ mediated lignin 5–5′ model molecule degradation.

Table 2
A brief summary of various lignin depolymerization methods.

	Methods	Advantages	Disadvantages
Thermochemical/Physical depolymerization	Pyrolysis	Rapid and easy to operate	Low selectivity in production, severe reaction condition and char formation
	Microwave-assisted	The operation can be precisely controlled and avoid surface heating	High energy consumption
Chemical catalysis	Acid-catalysis Base-catalysis	Effective and low cost	Environmental concern and corrosive acid catalysts may cause repolymerization
	Metallic-catalysis	High selectivity	Costly and low conversion rate
	Ionic liquid-catalysis	Highly adjustable reaction	Difficult to separate the product from the mixture
	Supercritical fluid-catalysis	Effective	Severe reaction condition
	Hydrogen peroxides catalysis	Low cost and facilely produce	Over-oxidation and low selectivity
Biological depolymerization	Bacteria conversion Fungal conversion	Eco-friendly and can be genetically engineered for specific chemical production	Low efficiency and long culture period
	In vitro enzyme depolymerization	Eco-friendly and can be used for various technical lignin purification	Low efficiency and seldom test with real lignin instead of a model molecule
	In vivo enzyme depolymerization	Eco-friendly and able to produce specific chemical	

LigE or LigF, cleave the β-O-4 ether bond and generate vanillin and α-glutathionyl-β-hydroxypropiovanillone (GS-HPV) as intermediate. Finally, the GS-HPV is oxidized by LigG, glutathione-S-transferase. The glutathione is cleaved and the remaining β − hydroxypropiovanillone can be further oxidized to vanillin [247,251]. After the genes of LigD, E, F and G have been identified, several genetic pathway studies have been conducted. Interestingly, Sonoki et al. expresses the LigD, F, G in the plant *Arabidopsis thaliana* and the result shows that the gene LigD, F, G can introduce post-lignification modification by cleaving several β-ether linkages and enhance the enzymatic digestibility of the lignin produced by the plant [252].

5.2.2.2. Bi-phenyl degradation pathway. The biphenyl linkage represents 10% of the total linkages in softwood lignin [3]. The purposed mechanism of biphenyl linkages degradation is shown in Fig. 14. When the 5, 5'-dehydrodivanillate (DDVA) enters the organism, LigX, a DDVA O-demethylase, can demethylate one of the methoxy group and convert it to the hydroxyl group [253]. The product of LigX is the substrate for oxidative meta-cleavage by LigZ, OH-DDVA dioxygenase [254]. The product from LigZ is further hydrolyzed by LigY, a hydrolase for the meta-cleavage compound of OH-DDVA. Finally, after the cleavage of LigY, 4-carboxy-2-hydroxypentadienoic acid and 5-carboxyvanillic acid (5CVA) are generated and 5CVA is further converted into one of the metabolic central products vanillate [251]. The cleavage of bi-phenyl linkage have been widely studied due to this structure is highly similar to polychlorinated biphenyls (PCB), one of the major pollutants and carcinogens from industrial production [255].

Even though the *in vivo* enzymes show great selectivity when compare to peroxidases and laccases, most of their reactions require ATP and NADH as cofactors to complete the reaction, and these requirements restrict their performance in industrial applications [251]. Furthermore, the conversion rate is significantly lower than other methods.

6. Summary

In this review, we summarize a series of methods for lignin depolymerization and conversion. Different methods have their own advantages and limitations. The comparisons of various methods are provided in Table 2. It is difficult to simply rank the best lignin depolymerization method among these treatments because their characteristic and products are various. Therefore, understanding the characteristic of each depolymerization methods and applying the appropriate approach for the specific purpose is the best treatment for lignin utilization.

In the point of view of lignin valorization, pyrolysis is the most effective method for converting lignin and biomass to crude bio-oil for energy generation. Moreover, during or after the pyrolysis, several value-added products can be recovered which can be used for lowering the energy production cost. However, in the case of depolymerizing lignin for specific valuable chemical production, chemical catalysis should be considered as the most appropriate approach due to the high specificity and conversion rate. Furthermore, the reaction condition of the catalysis is milder than pyrolysis which decreases the difficulty of handling the facility and reaction. Biological depolymerization is also a promising method for lignin valorization. However, it is still not close to actual application in industry and there are many challenges have to be solved before applying the enzyme or bacteria in lignin valorization. The major problem is the low efficiency of converting lignin polymer to monomers or even other chemicals. However, the study in biological lignin depolymerization is still meaningful and valuable because these technologies also can improve our waste treatment in the phenolic polymer. Furthermore, phenol-degrading enzyme and enzymes like β-etherase which has the ability to cleave ether linkage specifically are rare in nature. Comprehensive studies on these related enzymes could provide us an alternative and environmentally-friendly approach in various chemical treatments.

It is no doubt that biomass and lignin can be a promising alternative resource for replacing petroleum. Various studies have demonstrated the valorization of lignin by directly modifying lignin for multiple

applications. Numerous studies also show the potential of using lignin depolymerization for valuable chemical production. However, most of these studies are focusing on lab scale of experiments. The characterization of the products from the upgraded scale of lignin depolymerization can advance the process of utilizing lignin depolymerization in chemicals production. Furthermore, various studies also propose strategies for establishing a cost-effective and convenient system for lignin utilization. These afford would become the foundation of biomass utilization and green future.

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Declarations of interest

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