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Review on the preparation of fuels and chemicals based on lignin

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Lignin is by far the most abundant natural renewable aromatic polymer in nature, and its reserves are second only to cellulose. In addition to the rich carbon content, the structure of lignin contains functional groups such as benzene rings, methoxyl groups, and phenolic hydroxyl groups. Lignin degradation has become one of the high value, high quality and high efficiency methods to convert lignin, which is of great significance to alleviating the current energy shortage and environmental crisis. This article introduces the hydrolysis methods of lignin in acidic, alkaline, ionic liquids and supercritical fluids, reviews the heating rate, the source of lignin species and the effects of heating rate on the pyrolysis of lignin, and briefly describes the metal catalysis, oxidation methods such as electrochemical degradation and photocatalytic oxidation, and degradation reduction methods using hydrogen and hydrogen supply reagents. The lignin degradation methods for the preparation of fuels and chemicals are systematically summarized. The advantages and disadvantages of different methods, the selectivity under different conditions and the degradation efficiency of different catalytic combination systems are compared. In this paper, a new approach to improve the degradation efficiency is envisioned in order to contribute to the efficient utilization and high value conversion of lignin.

Introduction

With the depletion of non-renewable energy in nature and the excessive emission of greenhouse gases from petroleum materials, energetic and environmental problems are becoming increasingly acute. There is an urgent need for biomass with strong regeneration, clean, pollution-free and rich reserves in nature to be used as a substitute in the field of consumable fuel and petrochemical industry. China is a country with the largest energy consumption in the world, but the utilization rate of bioenergy is not high. In the same period, bioenergy accounts for only 0.1% of China's total energy consumption.[1] As we all know, lignocellulose widely exists in the waste of agricultural and forestry production, and it has great utilization value. Among them, the degradation and transformation of lignin has attracted much attention. Lignin is a natural renewable resource, second only to cellulose (see Fig. 1), also it has an

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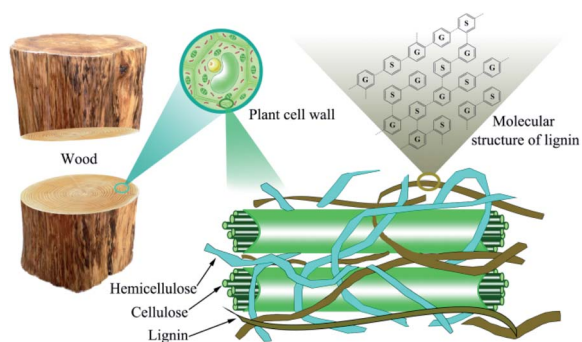
Fig. 1 Lignin structure of lignocellulosic biomass in wood.

aromatic structure that is rich in benzene rings, methoxy groups, phenolic groups, hydroxyl groups, carboxyl groups and other groups. It can expand the network and modify chemical sites of lignin to create higher value chemical products.[2] High value products such as bio-oil, chemical fuel, biochar and chemical monomers can also be obtained by pyrolysis and other degradation methods,[3] especially alkylated phenols after degradation, such as guaiacol, which are mainly used in industries such as antioxidants, spices, drugs or pesticides.[4] Therefore, the development and utilization of renewable lignocellulose resources to produce liquid fuels and bulk chemicals is of great significance to solve the resource and environmental crisis faced by human development, and alleviate people's excessive dependence on fossil resources.[5] The degradation of lignin is one of the effective methods to realize the high value transformation of lignin.

The main mode of bond breaking during lignin degradation is ether bond breaking (see Fig. 2).

According to the depolymerization mechanism, it can be divided into hydrolysis reaction, pyrolysis reaction, oxidation reaction, reductive hydrogenolysis reaction and biodegradation reaction. This paper reviews the latest research progress of lignin degradation methods in recent years from the aspects of hydrolysis, pyrolysis, oxidation, reduction and biodegradation (see Fig. 3).
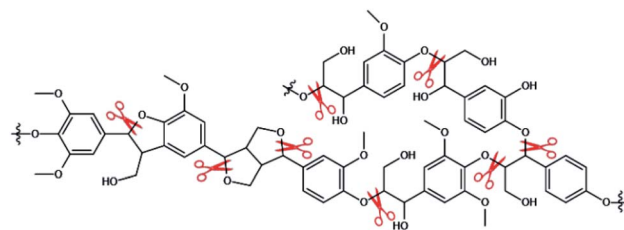

Fig. 2 Degradation mechanism of lignin macromolecules.

Industrial lignin is actually lignin separated from the original biomass raw materials in the process of extraction, pretreatment or other chemical activities. Here, it can be divided according to different treatment methods, mainly including sulfonated lignin, sulfated lignin, alkali lignin, organic solvent lignin, ammonia lignin, acid hydrolyzed lignin and ionic liquid lignin. On the other hand, for the division of natural lignin existing in biomass in its original form, it mainly includes milled wood lignin, enzymatic lignin and so on (see Fig. 4).

Hydrolysis

Among the lignin degradation methods, hydrolysis is a practical method with relatively mild reaction conditions. In the hydrolysis process, the catalyst is easy to disperse and the active sites of the catalyst are easy to contact β–O–4 bond. Compared with combustion and pyrolysis, lignin has high product selectivity in liquid phase environment. The main product is high-value small molecular phenolic products, which is a promising means of lignin depolymerization.[6]

Hydrolysis of lignin under acid condition

Under the catalysis of acidic conditions, lignin may break the C–O bond. Ito *et al.*[7] studied the acidic liquid catalytic reaction with lignin dimer as a model compound, and proposed a possible C–O bond breaking mechanism. The results showed

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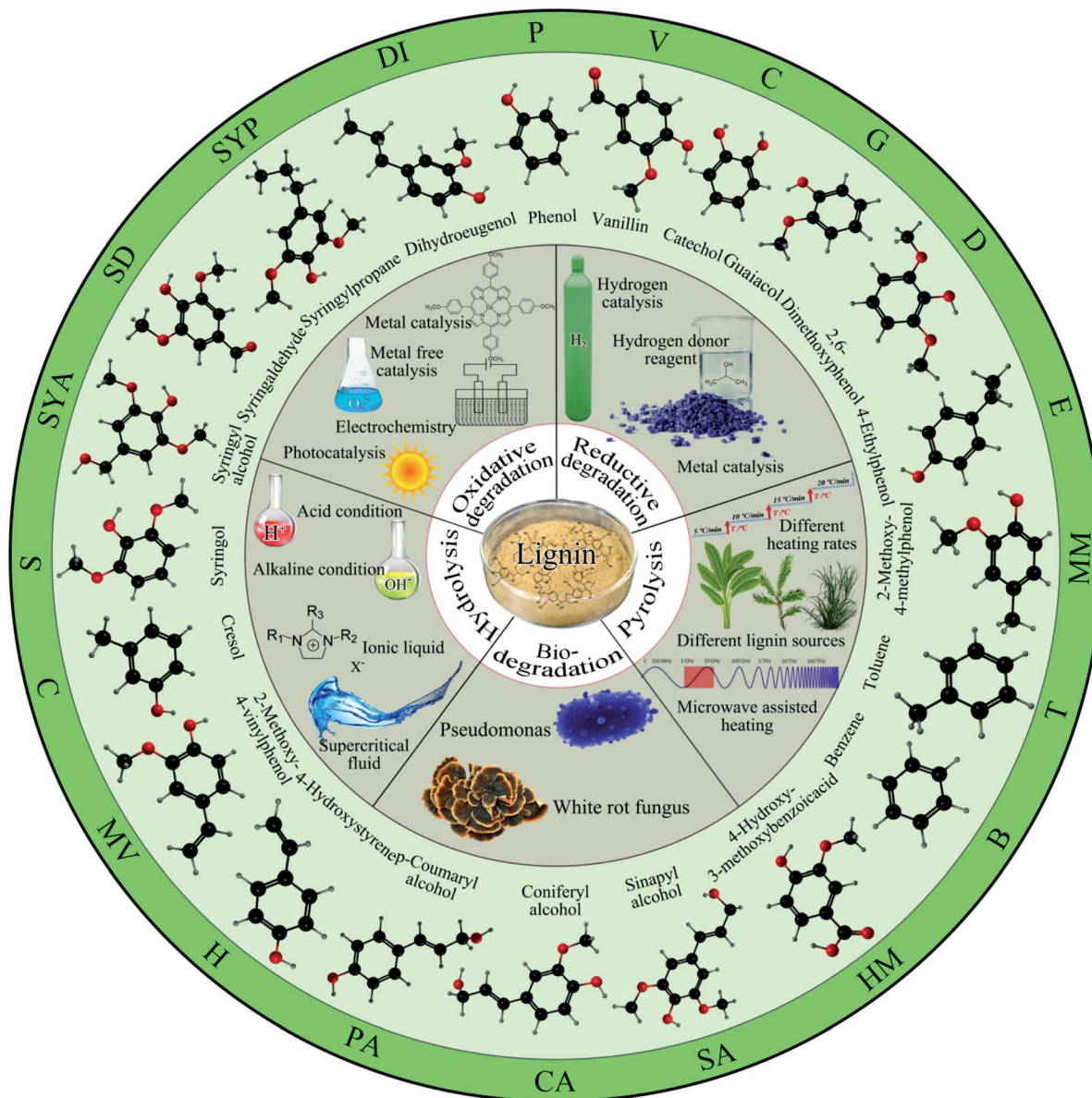
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Fig. 3 Lignin degradation method and its monomer. (The abbreviations corresponding to each monomer small molecule in the figure will appear in several tables below).

that strong acidic liquid conditions were required for the breakage of β–O–4.

Rahimi *et al.*[8] proposed a method for depolymerizing oxidized lignin under mild conditions of formic acid aqueous solution. This simple carbon oxygen cracking method can be used for depolymerization of poplar lignin to obtain low molecular weight aromatic compounds with a more than 60 wt% yield. Then Wang *et al.*[9] carried out the polymerization experiment of black liquor lignin under formic acid environment and microwave conditions. After 30 minutes of reaction at 160 °C, the highest yield of aromatics was 9.7%, which was more moderate and efficient than the electric heating method. Yang *et al.*[10] used an acidic catalyst (low acid amount) with a binary solvent to form a synergistic system to react the organic solvent lignin at a temperature of 200 °C for 60 min. The best

yields of liquid product and phenolic monomer were 67.4% and 27.7% respectively, showing the combination had good compatibility and recovery rate. The inorganic strong acid with high acidity can break the ether bond very well. Generally, the degradation activity of strong acid is from high to low: HI, HCl or H_2SO_4. Although these strong acids have high activity, they have disadvantages such as high cost and great harm.

Hydrolysis of lignin under alkaline condition

In alkaline medium, the ether bond in lignin macromolecules is easy to break, which promotes the degradation of lignin. Thring *et al.*[11] carried out experiments on lignin and its model compounds in alkaline solution, discovering that lignin was easy to degrade into guaiacol and purple eugenol under the
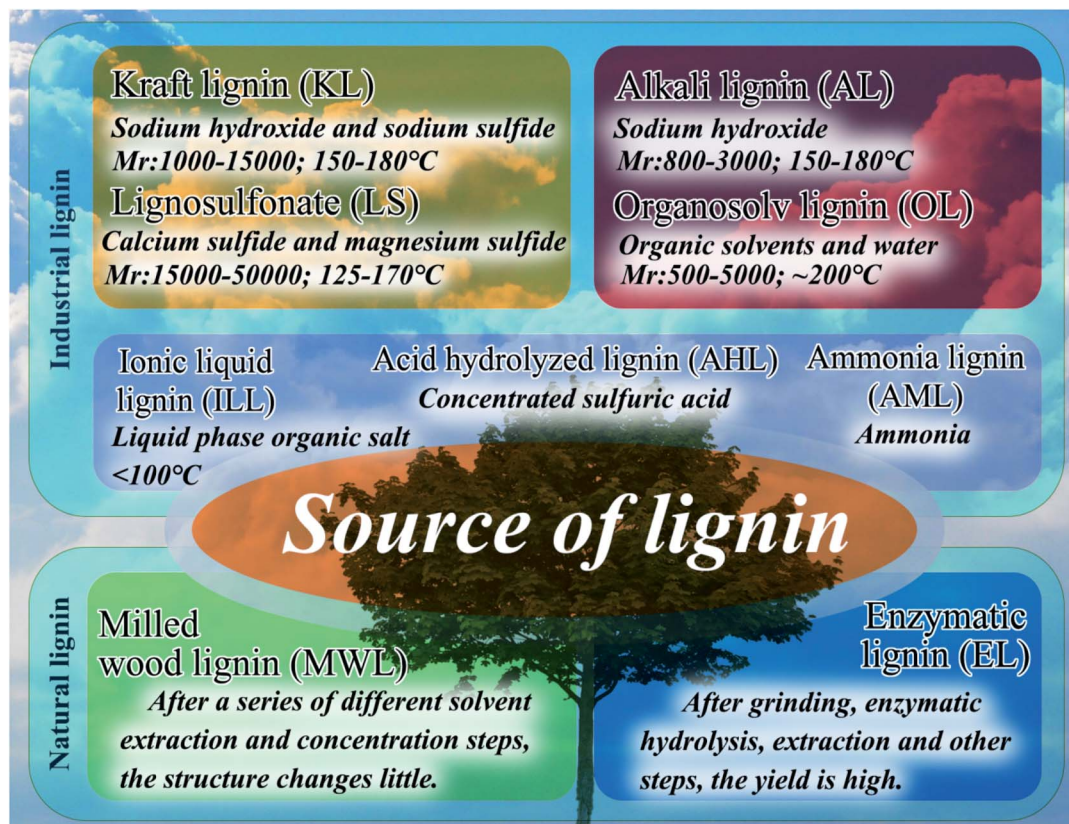
Fig. 4 Sources of lignin. (The abbreviations corresponding to each lignin source in the figure will appear in several tables below).

condition of low reaction temperature; at high temperature, the main degradation product is catechol. In different alkaline solution systems, the solubility of sulfate lignin decreased in the following order, LiOH > NaOH > KOH > CuAOH > TPAOH > TBAOH.[12] Therefore, the size of cation plays an important role in its solubility, and there are more simple aromatic compounds in the soluble part.[13] Under the existence of alkali metal carbonate, hydroxyl ions promote the activation of C_β–H bond. A single alkali metal ion interacts strongly with oxygen in the substrate, which is conducive to the polarization of ether bond. In $AlCl_3$ solution, water can form hydrogen bonds with oxygen atoms in phenethoxybenzene. This process is beneficial to C_β–O bonds' breaking, resulting in the production of phenol and 2-phenylethanol. $AlCl_3$ and Na_2CO_3 aqueous solution promoted proton assisted C–O bond breaking.

Hydrolysis of lignin under in ionic liquid

Ionic liquids can be regarded as the "green medium" for biomass conversion. In recent years, they have been used in the development and research of agricultural waste efficient utilization technology and new energy technology.[14] Ionic liquid is a kind of salt composed of cation and anion ions, existing in the form of melting at normal temperature and pressure. Ionic liquids have superior physical and chemical properties, such as low vapor pressure, high ignition point, difficult volatilization, excellent electrochemical performance and excellent solubility of organic and inorganic compounds.[15] Jia *et al.*[16] studied two

lignin model compounds with acidic ionic liquid 1-methyl-imidazole chloride as solvent and catalyst. The hydrolysis of β–O–4 bond showed that the alkyl aryl ether bond was broken in the depolymerization process, and the main product was guaiacol at 150 °C, with a yield of more than 70.0%. Xue *et al.*[17] used 1-methyl-3-benzylimidazole chloride and 1-methyl-3-benzylimidazole trichloroacetate to degrade and liquefy lignin. The liquefaction efficiency was up to 75.5%, and 60.0% of the low molecular products were phenols, reflecting the good selectivity of ionic liquid as a medium for the products. Cui *et al.*[18] prepared an imidazole cationic double salt ionic liquid in diethyl phosphate medium with catalyst hydrogen sulfate. Lignin was hydrolyzed under mild conditions to obtain value-added aromatics such as 2-methoxyphenol and vanillin.

Hydrolysis of lignin in supercritical fluid

Here, the supercritical fluid for hydrolyzing lignin mainly refers to supercritical ethanol or water and its combination of metal substances such as copper and ruthenium, or non-metallic substances such as carbon. In recent years, the degradation of lignin macromolecules in supercritical fluid has also become an effective way to produce lignin value-added products. Under supercritical conditions, water is similar to compressing dense gas to "dissolve" organic compounds and achieve the purpose of rapid degradation. Under supercritical conditions, inorganic substances such as salt are almost insoluble in water. Changing the temperature and pressure of water will change its physical

properties. Some organic reactions will be derived through supercritical reaction, such as oxidation reaction and hydrolysis reaction, then different ionic products will be generated. Organic substances can be completely transformed into carbon dioxide, water, etc.[19] Jiang et al.[20] hydrolyzed alkali lignin, xylitol residue lignin and ethanol residue lignin in supercritical water at 375 °C. The total phenol yield of corncob xylitol residue lignin was the highest, 140.0 mg g^{-1}, including phenol 28.9 mg g^{-1} and 4-ethylphenol 36.2 mg g^{-1}, with high selectivity. Kristianto et al.[21] degraded the lignin separated by concentrated acid hydrolysis of empty fruit string in supercritical ethanol, supplemented by formic acid medium and ruthenium/carbon as catalyst. The yield of bio-oil was 66.3 wt% and the content of aromatic monomer was 6.1 wt%.

Overall, lignin in acidic solutions, alkaline solutions, ionic liquids, low eutectic solvents, supercritical solvents, etc. generally require high temperature conditions with possible accompanying catalysts, but the reaction products of general acid–base systems have low yields and poor selectivity. Ionic liquids, low eutectic solvents are efficient depolymerization solvents,

they have good solubility for lignin, so the reaction efficiency is high. Ionic liquids are expensive and their performance is easily affected by impurities, while low eutectic solvents can be a good substitute for ionic liquids with cheap cost, stable performance and friendly to the environment. Finally, efficient solvent systems such as supercritical solvents are used to avoid the use of strong acids and bases so that the degradation reactions can be carried out under mild conditions and the product selectivity is not low. Industrial quality hydrolysis research progress as shown in Table 1 below.

Pyrolysis

Pyrolysis of lignin at high temperature will obtain hydrocarbons.[37] It is one of the main thermochemical methods to directly produce bio-oil from lignocellulose. Its mechanism is mainly that the phenylpropane structure of lignin is cracked into phenols, the side chain carboxyl group is cracked into CO_2, and the aromatic structure is carbonized into biochar.[38] Lignin pyrolysis bio-oil contains many useful chemicals, especially

Table 1 Progress in hydrolysis of industrial lignin from 2015 to 2021[a]

Raw materials	Lignin type	Solvent/catalyst	Reaction temperature (°C)	Productivity (wt%)	Main products after degradation	Ref.
Birch	OL	Water/Ru&Nb$_2$O$_5$	250	35.5	C$_7$–C$_9$ hydrocarbons	22
—	EL	Water/Ru&Nb$_2$O$_5$	250	99.6 (mol%)	C$_7$–C$_9$ hydrocarbons	23
Birch	OL	Water/Pd$_1$Ni$_4$/MIL-100 (Fe)	130–180	17.0	P, acetophenone	24
—	KL	Water–ethanol (1 : 1 v/v)	300	7.2 (Arene)	MM, C, G, etc.	25
Corn straw	—	Water–methanol (4 : 1 v/v)	260	14.77	E	26
—	AL	Ethanol/Ni–Co/activated carbon	280	18.2	Phenolic compounds (V, etc.)	27
Poplar wood	DL	Alkaline water/NiAl alloy	220	18.9	Aromatic monomers	28
—	BLL	Formic acid/microwave assisted	160	9.69 (Arene)	Apocynin, acetosyringone	9
Pubescens	OL	H$_2$O/ethane/formic acid/Pd/NbOPO$_4$	160	22.4	Aromatic monomers	29
Corncob residue	—	H$_2$O/tetrahydrofuran	300	24.3	Monophenols	30
—	KL	[DMEA][HSO$_4$]	160	59.18	V	31
—	OL	Propylene glycol ionic liquid	160	7.2 (Arene)	G, D, V, etc.	18
		Imidazole cationic double salt ionic liquid	160	10.6 (Arene)	G, D, 3,4,5-trimethoxybenzaldehyde, etc.	
Cassava Straw Bagasse Corn straw Corn cob	OL	BSbimHSO$_4$, N-butanol, water, N-hexane; water/ oil emulsion reactor	250	1.74 2.34 2.96 4.21 4.75	P, E, D, 4-ethylguaiacol	32
—	AL	[PrSO$_3$Hmim]$_2$[2HSO$_4$]	100	27.23	G	33
Corn cob	XRL	Supercritical water	375	2.89 3.62	P E	34
Poplar	AL			1.43 1.57	G D	
Empty fruit bunches	AHL	Supercritical ethanol, formic acid, Ru/C	350	6.1 (Arene)	P, methylphenol, ethylphenol, methoxyphenol, etc.	20
Oak	AHL	Supercritical ethanol	350	85 (Bio-oil)	Phenols, esters, furan, alcohols, etc.	21
Indulin AT™	KL	Supercritical ethanol/W–Ni–Mo/SEP trimetallic catalyst	280	41.41	Lignin oil (G and ethoxyphenol)	35
—	AL	Choline chloride and p-toluenesulfonic acid	130	52.14	DI	36
				8.83	4-Hydroxy-3-methoxy phenylacetone	
				6.73	4-Methoxy-3-hydroxyphenyl acetone	

[a] DL: dioxane lignin; BLL: black liquor lignin; XRL: xylitol residue lignin.

components with aromatic structure, which can be catalytically upgraded to many high value-added products.[39] The pyrolysis parameters and pyrolysis mechanism of lignin determine the distribution and properties of pyrolysis products. Heating degradation of lignin is conducive to further interpreting the original structure information of lignin and developing and producing energy sources such as sustainable bio-oil. In addition, the pyrolysis products of lignin are different due to the differences of heating rate, lignin type and other pyrolysis auxiliary conditions.

Effect of heating rate

Li et al.[40] studied the pyrolysis of lignin at different heating rates. At higher heating rates, the deoxidation reaction was inhibited with a short residence time, so that biochar had lower calorific value and energy yield. The heating rate would also affect the yield and distribution of pyrolysis oil. Li et al.[41] used moso bamboo as raw material, at the rate of 15 °C per minute, the total yield of small molecular products produced by carbohydrate degradation is 9.5 wt%, and the total yield of monophenol is 3.6 wt%. Galano et al.[42] explained from the perspective of kinetics and thermodynamics that the pyrolysis mechanism and kinetic parameters of lignin in the range of 200–350 °C are independent of temperature and conversion. The yield of aromatic and aliphatic products is affected by heat and mass transferring (e.g. heat transfer rate and residence time) in the gas phase; when the heating process is fast and the residence time is short, the relative amount of aromatic fragments is favorable. Yu et al.[43] pyrolyzed alkali lignin soluble and insoluble lignin separated from tetrahydrofuran (THF) at different temperatures and heating rates respectively. Heating rates and temperatures play an important role in the pyrolysis of lignin and biomass. In the temperature range of 450–525 °C, the amount of phenol is the highest in liquid products, while lower and higher temperatures promote the formation of dimers in liquid products.

Effect of lignin source

The pyrolysis technology of lignin has laid a foundation for expanding the application of lignin, but there are still many problems in practical application. For example, the structure of lignin, types of raw materials, processing and pretreatment have a direct impact on it. Lin et al.[44] conducted rapid pyrolysis research on milled wood lignin (MWL), enzymatic lignin (EL), alkali lignin (AL) and lignosulfonate (LS), the results showed that the pyrolysis behaviors of the four types lignin were very different. Phenols are the most abundant pyrolysis products of MWL, EL and AL. Sulfonate lignin will produce a large number of furan compounds and sulfur compounds. At 350 °C, the pyrolysis of EL produces mainly phenols, acids and alcohols. Research shows that the pyrolysis time does not affect the product distribution of EL. Júnior et al.[45] analyzed the pyrolysis of one commercial lignin and two lignin derived from paper-making process. The main pyrolysis products are phenolic compounds. At 650 °C, commercial lignin mainly produces hydrocarbons and phenols; industrial alkaline lignin mainly

decomposes into hydrocarbons and acidic compounds; industrial lignin with stronger acidity generates phenolic compounds at heating rate. Naron et al.[46] studied the catalytic pyrolysis of bagasse alkali lignin, eucalyptus sulfate lignin and pine sulfate lignin. At 250 °C and 350 °C, the catalyst impregnated with hydroxide will have different effects on the production and distribution of phenols depending on the type of lignin. The catalytic effect on pine is limited, but it can increase the phenolic yield of bagasse lignin by 26.0%, the phenol yield of Eucalyptus lignin can be increased by 40.0%, and the catalytic effect varies with the types of lignin. Zhang et al.[47] conducted rapid pyrolysis experiments with grass lignin, poplar lignin and sulfate lignin. Grass lignin can release more alkyl groups and produce the least amount of coke. Poplar lignin produces more kinds of pyrolysis products than grass lignin and has higher bio-oil production.

Due to the different conditions of lignin separation and extraction, it contains different bonds. The pyrolysis products and yields of different sources of lignin are different because they have different ratios of S, G, H units and different carbon–carbon and ether bond contents. The chemical reaction of lignin pyrolysis is very complex, and the breakage of carbon–carbon bonds is more tenacious than that of ether bonds, and methoxy is also more resistant. Therefore, high temperatures are required for carbon–carbon bond breaking and relatively low temperatures for ether bond breaking. In the whole depolymerization process, the reaction temperature range is wide, and the general trend of lignin degradation is similar for different species, but there are still obvious differences.

Influence of heating method

Compared with general heating degradation, the advantages of microwave pyrolysis include rapid and selective heating, improving energy efficiency and reducing cost. Microwave assisted pyrolysis can also specifically control pyrolysis parameters to maximize gas or oil production.[48] Bu et al.[49] used activated carbon as catalyst and microwave conditions to obtain the main chemical components of bio-oil, including phenols, guaiacol, hydrocarbons and esters (accounting for 71–87% of bio-oil). Bio-oil with high concentration of phenol (45.0% in bio-oil) can be obtained. The maximum calorific value of biochar obtained by lignin pyrolysis is about 24.0% higher than that of raw lignin. Xie et al.[50] used ZSM-5 supported cobalt catalyst to microwave pyrolysis bio-oil of lignin to obtain gases with main compounds of ketones, furans, phenols and guaiacols, as well as hydrogen and carbon monoxide. Bartoli et al.[51] studied the vacuum pyrolysis of sulfate lignin under microwave-assisted pyrolysis. Carbon was used as microwave absorber to obtain 37.0 wt% of bio-oil, mostly composed of high concentration of polysubstituted aromatic rings and light linear or cyclic compounds. Li et al.[52] used bagasse lignin and oxalic acid as catalysts to rapidly degrade lignin by microwave heating, and the liquefaction yield reached 78.7%. The microwave-assisted conditions can maximize the yield. The main chemical components of liquefied products include monosubstituted

and disubstituted phenol, which can partially replace petroleum phenol to produce phenolic resin adhesive.

Microwave conditions can be well applied to the depolymerization of lignin, which mainly plays an auxiliary role and acts as a "catalyst" to improve the degradation and conversion rate of lignin. The microwave magnetic field promotes the breaking of carbon–carbon bonds or ether bonds by generating thermal effect and non-thermal effect oscillation, so that the pyrolysis temperature does not need to be too high. Please see Table 2 below for the progress of industrial lignin pyrolysis research.

Oxidation

Compared with the above methods, the advantage of oxidative depolymerization of lignin is the high selectivity and high efficiency of lignin depolymerization products.[65] The products of lignin oxidative degradation are mainly low molecular weight phenolic compounds, which are mostly used to produce fine chemicals. In fact, oxidation method was used to study the macromolecular structure of lignin and the relationship between precursors as early as the 1970s.[66] In recent decades, various oxidation methods have been mature, including metal based catalysis, metal free catalysis, electrochemical catalysis and photocatalytic oxidation.

Table 2 Progress in (catalytic) pyrolysis of industrial lignin from 2015 to 2021[a]

Raw material	Lignin type	Reactor type	Reaction temperature (°C)	Yield (wt%)	Main products after degradation	Ref.
Corncob residue	OL	Fixed bed reactor	350	16.2 (Monomer)	H, MV	53
Cork	AL	Fixed bed reactor	650	54 (Bio-oil)	Aromatics	54
Douglas fir, radial pine	AL	Vertical pyrolysis furnace	600	5.02 (Monomer)	P, C	55
Corn cob	HL			20.48 (Monomer)		
—	AL	Microwave reactor	—	3.36 (±0.40)	P	56
				0.51	C	
				1.84	Methoxyphenol	
				0.50 (±0.04)	BTEXS	
—	AL	Pyrolysis gas chromatography/mass spectrometry	800	51.39 (Monomer)	P, C, dimethylphenol	57
				20.83 (Monomer)		
				18.01 (Monomer)		
Corn straw	AL	Fixed bed reactor	450	29 (Bio-oil)	H, MV	58
Radial pine	AL	Fluidized bed reactor	475	4.3 (Monomer)	G, eugenol	59
			525	6.8 (Monomer)	Alkylphenol, C	
			575	12.0 (Monomer)	Aromatics	
Maple	AHL	Pyrolysis gas chromatography/mass spectrometry	550	17.87	D	60
			650	14.47		
			550	13.05	Isoeugenol	
			650	14.14		
Straw			800	8.87	T	
			900	8.55		
Rice husk			800	7.73	T	
			900	9.47		
—	KL	Fixed bed reactor	500	~32 (Bio-oil)	Alkylphenol, aromatics, BTEX	61
			600	Selectivity 14.56	BTEX	
				Selectivity 13.35	Other aromatics, *etc.*	
Birch and poplar mixed	—	Fixed bed reactor	500	15.29 (Monomer)	Phenolic aromatic hydrocarbon	62
Eucalyptus				12.57 (Monomer)		
Black liquor	AL	Fixed bed reactor	600	20.34 (Bio-oil)	Monomer aromatics, polycyclic aromatic hydrocarbons, phenols	63
Corn cob	AHL	Fixed bed reactor	550	28.30	B, T, xylene	64

[a] HL: hydrolyzed lignin.

Metal catalysis

Kumar et al.[67] used copper and manganese bimetallic catalysts to study the effect of metal oxides on the yield of products. In the case of 50/50 (wt/wt) ethanol water co-solvent mixture, the maximum yield of bio-oil was 74.3 wt%. Among the catalysts used, Cu/γ-Al$_2$O$_3$ catalyst combined with 25/75 (wt/wt) ethanol water solvent can produce the largest amount of phenolic compounds (84.2%), showing that it is an excellent catalyst.

Metalloporphyrins, such as Mn, Ru, Co and other transition metal porphyrins, can catalyze the oxidation of hydrocarbons. The use of metalloporphyrins as selective oxidation catalysts can further promote the degradation of lignin to high-value chemical monomers. Xie et al.[68] degraded lignin in H$_2$O$_2$ menstruum with metalloporphyrin compound catalysis and microwave radiation. The results showed that cobalt porphyrin was helpful to improve the yield of aromatic monomers. Under the optimized conditions, with cobalt chloride as catalyst, the yield of aromatic monomers increased from 5.6% to 20.1%.

Co(salen), as a cobalt complex and dimeric peroxy compound containing oxygen molecules, has excellent oxygen carrying properties and can effectively oxidize lignin.[69] Zhou[70] further oxidized the lignin model with Co(salen) to benzaldehyde. On this basis, Zhou et al.[71] loaded Co(salen) on graphene oxide, showing the high breaking in lignin model compounds β–O–4 bond activity. The combined biomimetic catalyst Cu([H-4]salen)/Co([H-4]salen) can effectively oxidize organic solvent lignin, finding there is a high percentage of carbonyl compounds (84.6%) in the total degradation products. With the enhancement of Cu([H-4]salen)/Co([H-4]salen) catalysis, the degree of ether bond breaking increases.[72]

Xu et al.[73] designed a series of multiphase polyoxometalates with cesium exchange and transition metal substitution for the study of efficient catalysts for lignin depolymerization. 9.6% of monomer products can be produced in 3 hours under oxygen atmosphere of 150 °C. Under mild hydrothermal conditions, Tian et al.[74] synthesized a mixed valence copper polyvanadate based on copper organic skeleton with high catalytic activity and selectivity. Using NENU-MV-5 as heterogeneous catalyst and oxygen atmosphere, β–O–4 bond of lignin was oxidized and cracked into phenol and aromatic acid in one step.

Metal free catalysis

Metal free catalytic oxidation is a method of depolymerization of lignin. It can degrade lignin with oxygen molecules, hydrogen peroxide, ozone and some peroxy acids to produce chemical monomer products, such as aldehydes (vanillin, p-hydroxybenzaldehyde and syringaldehyde) or acids (vanillic acid and syringic acid). Aromatic compounds and aliphatic compounds with carboxylic acids can be prepared according to its oxidation degree.[75]

Kong et al.[76] used oxygen to catalyze oxidation, and the lignin in bagasse, poplar, bamboo and mango grass powder was degraded in the microemulsion reactor composed of octane, water and propyl alcohol. The yield of phenolic monomers was increasing significantly while the yield of p-coumarin was 6.1%. Li et al.[77] cracked in formic acid with H$_2$O$_2$ but not metal catalyst. After reacting at room temperature for 6 h, the yield of β–O–4 lignin model compound was more than 90.0%, and the catalytic effect was higher than that of oxygen. It was found that the in situ formed peracid could be used as the main oxidant. Musl et al.[78] treated sulfate lignin in alkaline solution with ozone. During the oxidation process, small molecular organic compounds were produced, resulting in the transfer of main active substances. The results showed that the carboxyl group in lignin polymer increased and the methoxy group decreased. Figueiredo et al.[79] depolymerized various residual lignin in the micro reactor device with ozone and without catalyst. The generated products include carboxylic acid, methyl ester and acetal, and the depolymerization of organic solvent lignin is up to 70.0%, with ideal degradation effect. Bu et al.[80] pretreated bagasse with peroxyformic acid. Under the optimized pretreatment conditions, the lignin degradation rate reached 59.0% and the its effect was good.

The reaction conditions for oxidative degradation of lignin are generally mild, and good degradation can be achieved without the use of high temperatures. Non-metallic oxidative degradation has low efficiency, low product selectivity and complex composition. Metal oxidation can improve the product yield and selectivity, but the metal catalyst preparation is more complicated as well as the loading of precious metals, which may cause high cost.

Electrochemical degradation

Electrochemical degradation is a green catalytic oxidation method. It is one of the most promising methods for efficient and sustainable conversion because of the availability of electron gain/loss transfer instead of redox reagents.[81] Electrons can catalyze redox reactions by replacing expensive and complex redox reagents with current. The catalytic effect of electrochemistry has little relationship with concentration and temperature. The energy of electrons can be determined by external electric field. Most electrocatalytic oxidation reactions are carried out at room temperature without additional heating. The electrode plays the role of "catalyst" in redox and can act as homogeneous and heterogeneous catalysts.[82]

Ghahremani et al.[83] designed a nickel cobalt bimetallic electrocatalyst for electrochemical oxidation of lignin. The research shows that the catalyst has a high electrochemical oxidation rate of lignin, and its degradation products mainly include vanillin, vanillin acetophenone and 3-methylbenzaldehyde. Chang et al.[84] prepared an electrochemically treated titanium dioxide nanotube electrode to study the effect of tube length on lignin electrooxidation efficiency. After the treatment, a significant increase in lignin oxidation efficiency was observed. Zirbes et al.[85] degraded sulfate lignin by electrooxidation in a high temperature electrolytic cell at 160 °C. The results showed that the selectivity of vanillin was 67.0% higher than that of nitrobenzene oxidation.

Photocatalytic oxidation

Photochemical process, especially heterogeneous photocatalytic processes involving semiconductors and UV radiation,

Table 3 Progress in oxidation of industrial lignin from 2015 to 2021

Raw material	Lignin type	Oxidant	Reaction temperature (°C)	Solution	Catalyst	Productivity (wt%)	Main products after degradation	Ref.
Cork	AL	H2O2	80–120	1-Ethyl-3-methylimidazole acetate solution	Nb2O5 CoCl2	0.26–0.99 0.41–0.90	G, SYA, V, acetovanillone, homovanillic acid	91
—	Dealkylated lignin	O2	160	NaOH	LaFe$_{0.2}$·Cu$_{0.8}$O$_3$	10.0	SD	92
—	KL	O2	120	Phenol	ReO$_x$/γ-Al$_2$O$_3$	7.3	V	93
Black liquor	AL/KL	TEMPO/Cu(OAc)$_2$	110	Ionic liquid (ammonium 2-hydroxyethyl formate)/formic acid and sodium formate		75	Ethyl acetate soluble product	94
—	Supercritical hydrolysis of lignin	TEMPO, HNO$_3$/HCl, O$_2$	150	Methanol	Polyoxometalates	19.4	Aromatic monomer	95
Bagasse, poplar, bamboo or Miscanthus powder	OL	O2	160	Water, n-octane, n-propanol	CuSO$_4$	6.09 ± 0.38 2.37 ± 0.25 0.56 ± 0.08	PA CA SA	96
Poplar	—	O2	190	Buffer and NaOH	CuSO$_4$	7.8 23.4	V SD	97a and 97b
Pine	KL	Nitrobenzene	180	NaOH	—	10.9	V	98
Cryptomeria japonica	Soda anthraquinone lignin	Nitrobenzene	180	NaOH	—	8–11.2	V	98
Cryptomeria japonica	Extraction of lignin with neutral solvent	Bu$_4$NOH aqueous solution	120	NaBr, NaCl, NaOH, Na$_2$SO$_4$	Bu$_4$NCl	21.0 1.7	V HM	99
Straw	AL	Battery anode stainless steel	25	NaOH	Current density: 50 mA cm^{-2}	6 (Vanillin)	V, acetosyringone, phthalic acid	100
Black liquor	KL	Battery anode nickel base material	80	NaOH	Current density: 1.9 mA cm^{-2}	0.34 mg ml^{-1} (Vanillin)	V, HM, acetovanillone	101
—	KL	Battery anode nickel base material	80	Strong alkaline electrolyte, desorption of ethyl acetate and acetic acid	Current density: 38 mA cm^{-2}	1.3	V	102
—	KL	—	—	Acetonitrile and deionized water	TiO$_2$: lignin = 1 : 0.5	1.68	V	103
—	AL	H2O2	27	H$_2$O	UV-vis radiation	—	About 64% reduction in COD values	104

such as titanium dioxide/UV, Fe_2O_3 titanium dioxide/UV, zinc oxide/UV, zinc oxide/O_2/UV and titanium dioxide/H_2O_2/UV,[86,87] have also been widely used in the field of lignin degradation.

Gong *et al.*[88] carried out the experiment of Bi and Pt promoting the oxidation of LS on the surface of titanium dioxide under certain conditions. Bi/Pt–TiO_2 photocatalyst showed excellent reactivity in producing high-value compounds and CO_2 in the process of oxidizing lignosulfonate. About 85.0% of lignosulfonate was converted to guaiacol, vanillic acid and vanillin. Kärkäs *et al.*[89] developed a catalytic scheme to oxidize lignin model system by combining photooxidation and palladium catalysis, which can effectively oxidize lignin model substrate at room temperature and obtain high yield of oxidation products. Chu *et al.*[90] prepared a metal derived photocatalyst that interacted with visible electromagnetic spectrum light to oxidize commercial lignin. The obtained oxidation products contain vanillic acid, ferulic acid, benzoic acid and *p*-coumaric acid, accounting for about 85.0% of the detectable lignin oxidation products, and the pretreatment effect is excellent. Research progress of oxidative degradation of industrial color quality as shown in Table 3 below.

Reduction

Reductive depolymerization of lignin is usually carried out in the presence of various carriers, reducing agents and solvents.[105] The aromatic structures of lignin contain very complex bonds, different phenolic units pass through C–O–C bonds (β–O–4/4′, α–O–4/4′, α/γ–O–γ, 4–O–5/5′, *etc.*) and C–C bond (5–5/5′, β–β, β–1, β–5) isosemirandom crosslinking.[106] Reductive degradation is a degradation method in which the ether bond in lignin breaks under the action of hydrogen source and catalyst. The degradation products are mainly phenolic compounds and lignin oligomers.

Hydrogen reduction

When hydrogen is supplied as a gas, the process is usually called hydrotreating. Wang *et al.*[107] prepared carbon modified nickel catalyst by carbothermal reduction method, studying its catalytic oxidation and hydrogenolysis of lignosulfonate. The reaction was carried out at 200 °C, 1 MPa H_2, finding the total yield of aromatics could reach 22.0%. Qi *et al.*[108] also adopted the method of combining oxidation and hydrogenolysis. After hydrogen peroxide destroyed the hydrogen bond of sulfate lignin, gaseous hydrogen was used as hydrogen donor for catalytic hydrogenolysis in the presence of nickel catalyst supported on ZSM-5 zeolite. The conversion of sulfate lignin to monomer exceeded 83.0 wt%, and the conversion of charcoal decreased to 8.0 wt%. Konnerth *et al.*[109] studied the promotion of alkali in the metal catalyzed hydrogenolysis of lignin model compounds and organic solvent lignin. Using gaseous hydrogen as hydrogen donor, it was found that the presence of alkali had a positive selective response to monomer compounds, and the yield of monomer aromatic compounds obtained from lignin also increased significantly. The total conversion of Rh/Nb_2O was 99.3%, of which the aromatic products were about 98.9%.

Rh particles are responsible for the dissociation of H_2 and NbO_x to activate the C–O single bond. The conversion of lignin into valuable aromatic compounds under low hydrogen pressure provides a broad prospect.[110]

Reductive catalytic fractionation (RCF) of lignocellulose over heterogeneous catalysts can effectively recover high-yield phenolic monomers. Wang *et al.*[133] conducted reduction experiments on birch on N-doped carbon-supported catalysts. At 250 °C, 3.0 MPa, under the initial H_2 pressure, the yield of lignin-derived phenolic monomeric carbon is 52.7C%.

Hydrogen donor reduction

In addition, hydrogen has poor solubility in most solvents, and high-pressure molecular hydrogen needs to be directly used in the hydrogenolysis process, bringing disadvantages including purchase, transportation, expensive infrastructure and potential safety hazards. Catalytic transfer hydrogenation is a green alternative method, which is based on hydrogen supply solvents, such as methanol, ethanol, isopropanol, formic acid, tetrahydronaphthalene, *etc.* The advantage of this method is to avoid the use of high-pressure hydrogen and other explosive gases.

Wang *et al.*[111] revolutionized the technique of lignin depolymerization and removal of oxygen-containing functional groups by applying the catalyst RANEY® Ni to the hydrogen transfer reaction of lignin model molecules, using isopropyl alcohol as the hydrogen transfer initiator and hydrogen transfer propagator. This reaction exhibited good hydrogenolysis and regenerative stability at 80–120 °C, which transformed lignin into low boiling point aromatics. Cheng *et al.*[112] reductively degraded lignin in ethanol and isopropanol solvents. At 270 °C, the highest yield of phenol monomer obtained on $Ni_{10}Cu_5$/C catalyst is 63.4 wt%, with remarkable selectivity. The lignin dimers may include diphenylethane type, phenylcoumarin and terpineol. Shimanskaya *et al.*[113] synthesized palladium containing catalysts in the presence of isopropanol. Lignin degradation produced aromatic compounds, mainly benzene and toluene. When supercritical isopropanol was used, the maximum conversion of lignin reached 50.0%, and the maximum selectivity of the catalyst to aromatics was more than 70.0% when supported on super crosslinked polystyrene.

Other catalytic reduction methods

Ouyang *et al.*[114] studied the three-step method to obtain monomer alkylmethoxyphenol from pine wood rich in guaiacol lignin by platinum/carbon catalyzed reductive depolymerization. In the second step, the methoxy groups in these lignin monomers were selectively removed by using the optimized mop/silica catalyst to generate 4-alkylphenol, and the alkyl groups catalyzed by zeolite were transferred to the benzene stream for dealkylation. Based on the initial lignin content in pine wood, the total yield of phenol can reach 9.6 mol%. Verziu *et al.*[115] explored the catalytic performance of nickel and ruthenium catalysts for the reductive depolymerization of Miscanthus lignin. The presence and oxidation state of ruthenium, and the content of nickel have an impact on the

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Table 4 Progress in reduction of industrial lignin in 2015–2021

Raw material	Lignin type	Solvent	Catalyst/additive	Temperature (°C)	Time (h)	Gas pressure (bar)	Monomer yield (wt%)	Main products after degradation	Ref.
Beech	OL	Water	RANEY® Ni	360	3	70 (H$_2$)	10.1	P, 4-propylphenol	117
Birch	OL	Methanol	Ni$_1$–Fe$_1$/AC	200	6	20 (H$_2$)	20.3	DI, SYP	118
Oak	OL	Methanol	Pd/C	180	2	30 (H$_2$)	25.0	DI, SYP	119
Corn cob	OL	Methanol	ZnMoO$_4$/MCM-41	220	4	30 (H$_2$)	14.3	Methyl ferulate, methyl coumarate	120
Poplar	AML	Water/methanol (1:1, v/v)	Pt/Al$_2$O$_3$	300	2	30 (H$_2$)	18.9	D, SYP, 2,6-dimethoxy-4-[(1E)-1-propen-1-yl]phenol, 4-(3-hydroxypropyl)-2,6-dimethoxyphenol	121
Empty fruit bunches	OL	Water/ethanol (7:13, v/v)	Ru/H$_\beta$	225	6	40 (H$_2$)	16.5	DI, isoeugenol	122
Moso bamboo	OL	Water/ethanol (6:4, v/v)	Pd/NbOPO$_4$	100	20	20 (H$_2$)	22.4	D, E	74
Bagasse	OL	Isopropyl alcohol	Ni/ZrP	260	4	20 (H$_2$)	15.1	E	123
Bagasse	OL	Isopropyl alcohol	Ni/MgO	270	4	30 (H$_2$)	15.0	E	124
Corncob residue	OL	Water/N-butanol (4:6, v/v)	Ni/HZSM-5	300	4	20 (H$_2$)	19.5	E, 4-ethylguaiacol	125
Bagasse	OL	Methyl isobutyl ketone	H-USY	350	1	20 (H$_2$)	19.4	P, G, E	126
Cork	KL	Water	NiMoS$_2$/C	300	5	30 mL min^{-1} (H$_2$) Ar : H$_2$ (1 : 2)	—	Organic acid	127
Birch	LS	Methanol	Ni/MgAlO–C	200	6	10 (H$_2$)	22	Aromatic mixture	128
—	Indulin AT™	Water	S$_2$O$_8^{2-}$/ZrO$_2$–TiO$_2$–SiO$_2$/Pt/C	270	1	20 (H$_2$)	6.81	Aromatic compounds	129
—	OL	Ethanol	Pd/C	400	—	50 (H$_2$)	13.5	2-Propylresorcinol and 2-ethylcatechol or 3-methoxycatechol, 4-methylcatechol (without the catalyst)	130
Sorghum straw	AHL	Ethanol	Ni/Al-SBA-15(20)	280	4	10 (H$_2$)	17.83	G, phenolic monomer	131
Poplar	AHL	Water/methanol (3:7, v/v)	Pd/C	200	3	20 (H$_2$)	35.5	4-(3-Hydroxypropyl)-2,6-dimethoxyphenol	132
Castor seeds	C-lignin	Methanol	Ru/ZnO/C	200	4	30 (H$_2$)	51	Propenylcatechol	133
Birch	—	Methanol	Pd$_{0.25}$/CN$_x$	250	3	30 (H$_2$)	52.7C%	Phenolic monomers	134
Birch	OL	Water/ethanol	Ru@NCM-800	300	2	10 (H$_2$)	30.5	Aromatic monomers	135
Switchgrass	ILL	Isopropyl alcohol	5% Ru/C	300	3	20 (N$_2$)	27	4-Ethylguaiacol, 2,6-dimethoxy-4-[(1E)-1-propen-1-yl]phenol, isoeugenol	136
Sorghum	DES lignin	Isopropyl alcohol	5 wt% Ru/C	270	1	N$_2$	27.39	P, E, 4-ethylguaiacol, DI	137
—	KL	Isopropyl alcohol/water	Rh/La$_2$O$_3$/CeO$_2$–ZrO$_2$ + Fe	373	2	—	26.4	—	138
—	LS	Water/n-butanol/isopropyl alcohol (1:1:3, v/v/v)	RANEY® Ni	200	2	10 (N$_2$)	11.6	4-Ethylguaiacol	139
Corn straw	EL	Isopropyl alcohol/water (2:1, v/v)	Ni$_{50}$Pd$_{50}$/SBA-15	220	8	5 (N$_2$)	8.14	E, 4-ethyl-2,6-dimethoxyphenol, SYP	140
Birch	AHL			245	8		18.52	SYP	
Beech	OL	Isopropyl alcohol	Ni/Al$_2$O$_3$	170	12	10 (N$_2$)	13.4	2,6-Dimethoxy-4-[(1E)-1-propen-1-yl]phenol, SA, CA	141
—	KL	Ethanol	Ru/C + MgO/ZrO$_2$	350	1	10 (N$_2$)	7.32	Butyl hydroxyanisole, 2-methoxy-2-phenylethanol	142
Straw	AL	Supercritical ethanol	Cu/ZSM-5(30)	440	5	10 (N$_2$)	98.2	Monoaromatic compound	143
Poplar	OL	Acetone/isopropyl alcohol	ZnIn$_2$S photocatalyst	42	24	Ar	10	p-Hydroxyacetophenone derivatives	144

Table 4 (Contd.)

Raw material	Lignin type	Solvent	Catalyst/additive	Temperature (°C)	Time (h)	Gas pressure (bar)	Monomer yield (wt%)	Main products after degradation	Ref.
Birch	AHL	Methanol/water (1 : 2, mol mol^{-1})	Pt/γ-Al$_2$O$_3$	230	3	30 (N$_2$)	46.1	4-Propyl-syringol	145
Birch	Untreated	Water/ethanol (1 : 1, v/v)	Co o-phenanthroline/C	200	4	Ar	15 / 11	4-Propyl-syringol / 4-Propenyl-syringol	146
Poplar	OL	Ethanol/isopropyl alcohol	Ni$_{10}$Cu$_5$/C	270	4	10 (N$_2$)	63.4	DI, SYP	147

depolymerization performance of lignin. Ruthenium loaded on alumina will lead to lignin degradation rate of up to 89.0%. In addition, due to the synergistic effect of bimetallic, the best selectivity is obtained in the production of dimer. Zeng et al.[116] prepared highly dispersed iron palladium bimetallic catalyst by impregnation method. Under the optimal reaction conditions in ethanol water solvent, the hydrogenolysis conversion of lignin is as high as 98.2%, the yield of aromatic monomer is 27.9%, and the hydrogenolysis effect is good. Research progress on reduction and degradation of industrial dyes, see Table 4.

Biodegradation

The biodegradation of lignin is mainly completed by the synergistic action of bacteria and fungi, in which fungi are considered to be more effective in the decomposition of lignin.[148] For example, white rot fungi can decompose lignin with the help of extracellular peroxidase and laccase, and can preferentially degrade lignin rather than cellulose.[149] Su et al.[150] degraded corn straw under the action of fungus granula verrucosa. After two weeks, it was found that 49.9% of lignin had been depolymerized. Similarly, Tišma et al.[151] used silage corn as raw material to explore the degradation effect of white rot fungus *Chaetomium versicolor* on lignin. Co-digestion and incubation with cattle manure at 27 °C for 7 days, the degradation rate was up to 70.0% with excellent results.

The fungal degradation of lignin has been fully studied, but the catabolic pathway of lignin degraded by microorganisms is still incomplete, mainly because lignin contains complex mixture of components and is difficult to decompose. In the catabolic pathway of lignin component degradation, bacteria and fungi also have diversity. It seems that there are more possible interactions between enzymes and metabolic pathways and microorganisms to be studied.[152] The whole lignin catabolism system is redundant and complex, but the correct interpretation of the system will be important for the development of lignocellulose biorefinery. Research progress of industrial quality biodegradation see Table 5.

Applications of depolymerization monomers

Lignin can be used as a high value fuel after degradation and the density of some of the fuels is very close to petroleum based high density jet fuel. Preparation of high density and low freezing point biomass-based jet fuels from lignin is still to be developed.[164]

Dai et al.[165] applied Foucault alkylation reaction by utilizing lignin phenolic monomers, aldehydes and ketones intermediate small molecules (guaiacol and propionaldehyde) as raw materials, finally obtained long-chain alkane fuels. Nie et al.[166] performed acid-catalyzed alkylation of lignin-derived phenols (phenol, anisole, guaiacol) with benzyl ether or benzyl alcohol. The alkylation products were hydrogenated in the presence of Pd/C and HZSM-5 to obtain biofuels with densities up to 0.93 g mL^{-1} and freezing points as low as -40.0 °C, comparable to the

Table 5 Progress in biodegradation of industrial lignin in 2015–2021

Raw material	Lignin type	Microorganism	Strain	Degradation time (d)	Degradation (%)	Ref.
Broad-leaved trees	Sodium sulfite treatment	Bacteria	*Brevibacillus thermoruber*	7	82.0	153
—	AL	Bacteria	*Pseudocitrobacter anthropi* MP-4	7	52.1	154
Switchgrass	—	Bacteria	A novel multi-copper polyphenol oxidoreductase (OhLac)	3	6.2	155
Corn stalk					5.2	
Wheat straw					4.3	
Corn straw	—	Bacteria	*Enterobacter hormaechei* KA3	7	32.1	156
Pulp and paper effluent	—	Bacteria	*Brevibacillus parabrevis* MTCC 12105	6	53.8	157
Wheat straw	—	Fungi	*Pleurotus ostreatus*	15	16.8	158
			Trametes versicolor		6.1	
			Pleurotus eryngii		7.6	
Corn stover	—	Fungi	*Myrothecium verrucaria*	14	49.9	159
Radiata pine	—	Fungi	*Trametes versicolor*	21	16.0	160
			Stereum hirsutum	21	16.0	
Corn silage	—	Fungi	*Trametes versicolor* & cow manure	7	70.0	151
—	KL	Fungi	*Phanerochaete chrysosporium* & *Irpex lacteus*	21	26.4	161
Black liquor	—	Fungi	*Daldania eschscholtzii* SA2 146	7	15.0	162
—	Dealkaline lignin	Fungi & electro-fenton reaction	*L. Edodes* & optimal voltage (4 V)	4	89.0	163

widely used JP-10 fuel, they had good low-temperature properties. Deng *et al.*[167] used catalytic hydroxyalkylation/alkylation of lignin-derived cyclohexanone with hemicellulose-derived 2-methylfuran to produce high-density biofuel precursors. The amberlyst-15 catalyst, low FC/cyclohexanone ratio and the presence of aqueous solvent were used. After hydro-deoxygenation, high density biofuels with a density of 0.825 g mL^{-1} were obtained. Xu *et al.*[168] extracted methylbenzaldehyde and cyclohexanone from lignocellulose to develop jet fuel, the obtained 1-methyldodecahydro-1*H*-fluorene and 3-methyl-dodecahydro-1*H*-fluorene had high density (0.99 g mL^{-1} and 0.96 g mL^{-1}, respectively). Nie *et al.*[169] used a hydrophobic acidic resin (Rx) to catalyze a lignocellulose-derived mixture and obtained a product yield of 75.4% in the co-conversion of lignocellulosic derivatives. After hydrodeoxygenation, a jet fuel blend with higher density and excellent freezing point than JP-7 was obtained.

As previously described, phenol, anisole, guaiacol, cyclohexanone, and methylbenzaldehyde are small molecule products of lignin degradation, the hydroxyl and methoxy groups of lignin-derived small molecules can provide electrons to the benzene ring, which will later be activated to undergo alkylation with alkanes, alkenes, alcohols, ethers, and ketones.[166,170] Therefore, lignin degradation products can be used as feedstock for the economic synthesis of high-density biofuel precursors.

Conclusions

Hydrothermal degradation is common in the pretreatment of lignin. Generally, it should be degraded together with oxidation–reduction or completely degraded under microwave and other auxiliary conditions. The yield of hydrolysis is low and it is difficult to degrade into monomers in one step; in the process of pyrolysis, the product surface is easy to coke, resulting in poor product selectivity, so the requirements for equipment are high. Besides, the pyrolysis oil is highly oxidized and unstable. Redox degradation law is based on the molecular bond of lignin macromolecules, which is directional and efficient. However, there are still many shackles in industrial application, such as secondary polymerization and difficult separation of products. The cost of noble metal catalysis in oxidative degradation, efficiency of photocatalysis, the complexity of electrochemical catalysis and the safety of hydrogen in reductive degradation are also the defects of such methods. The advantage of biodegradation is green and it does not consume reagent materials, nevertheless, it needs bacteria selection, culture and other links in the process. Biodegradation has a long cycle and slow effect, it means that it is not suitable for large-scale production and is not conducive to practical application. Therefore, if lignin needs pretreatment, it can be considered to reduce the degree of polymerization, which is conducive to the next step of catalysis. In the aspect of lignin hydrolysis, reaction media such as green solvent ionic liquid, low eutectic solvent and supercritical fluid can be introduced to design ionic liquid with specific physical and chemical properties and binary solvent synergistic reaction; in terms of pyrolysis, microwave heating and other auxiliary conditions can be used to reduce energy consumption, or green alcohol based solvents can be added to inhibit the repolymerization reaction; when hydrogen donor reagent are used as hydrogen donors or lignin derived alcohols or acids are utilized instead of hydrogen as hydrogen donors to realize green "self-produced" reduction, the design of efficient catalysts in place of precious metals not only focuses on carbon–oxygen bonds, but also the fracture of carbon–carbon bonds.

In conclusion, the degradation of lignin is one of the ways to realize the high-value utilization of lignin, it is also a hot and difficult point in the research of renewable resources for petrochemical alternative products. It is believed that the degradation system of lignin and the application expansion of its degradation products will be continuously enriched and improved in the near future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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