

Catalytic Hydrogenolysis Lignin to Obtain Phenols: A Review of Selective Cleavage of Ether Bonds

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Lignin depolymerized phenolic compounds and biofuel precursors are ideal value-added products for lignin residues generated in biorefineries and modern paper pulp facilities. Hydrogenolysis of lignin is an efficient depolymerization method for the production of carbon-neutral sustainable fuels and platform chemicals. Lignin is underutilized due to its complex structure, mainly because of its complex interunit linkage crosslinks such as α -O-4, β -O-4, 4-O-5, and β -5. This paper centers on the hydrolysis reaction of three major ether bonds (α -O-4, β -O-4, 4-O-5) in lignin and lignin model compounds based on different catalysts for hydrogenative degradation and catalytic systems. The methods and strategies to inhibit the condensation reactions are summarized. In particular, density functional theory calculation of the reaction pathways are combined with isotopically labeled reaction pathways to deeply analyze the hydrogenation degradation mechanism of biomass and further improve the yield of monophenols during the hydrogenation degradation of lignin. Finally, a brief summary of the challenges and prospects of lignin hydrogenation degradation is proposed.

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INTRODUCTION

With the consumption of fossil energy and environmental pollution, the fluctuation of fossil energy prices also brings negative effects on economic development. In response, the Chinese government has proposed to accomplish the tasks of achieving carbon peak and carbon neutrality, as well as optimizing the energy structure. In order to achieve this goal, biomass stands out from a variety of renewable energy sources and can play a huge role in the development of clean energy due to its sustainable and carbon-neutral properties. But for now, the direct use of biomass for mass production of fine chemicals or energy without competing with food supplies remains one of the major challenges of sustainable chemistry. Aiming to successfully address this challenge, it is necessary to upgrade traditional chemical catalysis methods. Novel methods are needed to depolymerize and de-functionalize complex lignin structures as a way to obtain a variety of platform chemicals (Wendisch *et al.* 2018; Süß *et al.* 2022). Because traditional petroleum-based chemicals mainly add functional groups to simple structures, this approach is obviously unreasonable for biomass-based chemical production processes. To take advantage of all lignocellulosic components, special attention must be paid to the depolymerization of lignin, which has proven particularly difficult. This review will outline the research progress of

hydrogenation-facilitated degradation of lignin. The focus will be on the three main ether bonds hydrogenolysis reactions, aiming to obtain simple platform compounds, while also providing strong support for lignin depolymerization.

Biomass resources are generally composed of 30 to 50% cellulose, 20 to 35% hemicellulose, and 20 to 35% lignin (Leng *et al.* 2022). Due to its complex three-dimensional mesh structure, compared to cellulose and hemicellulose, lignin is the most difficult to utilize, but its aromatic structure has attracted the attention of more and more researchers. In nature, lignin is biosynthesized from three simple aromatic substances: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These monomers are randomly coupled through a free-radical process to form a stable, non-uniform, three-dimensional biopolymer that is particularly resistant to chemical degradation. These three monomers are often linked by ether bonds and carbon-carbon bonds. Among them, the ether bond as a chemical bond with weak bond energy in lignin has been studied by a large number of scholars. Ether bonds in lignin generally include α -O-4, β -O-4, and 4-O-5 (Lei *et al.* 2019). The structure of these three ether bonds and their relative contents in lignin are shown in Fig. 1.

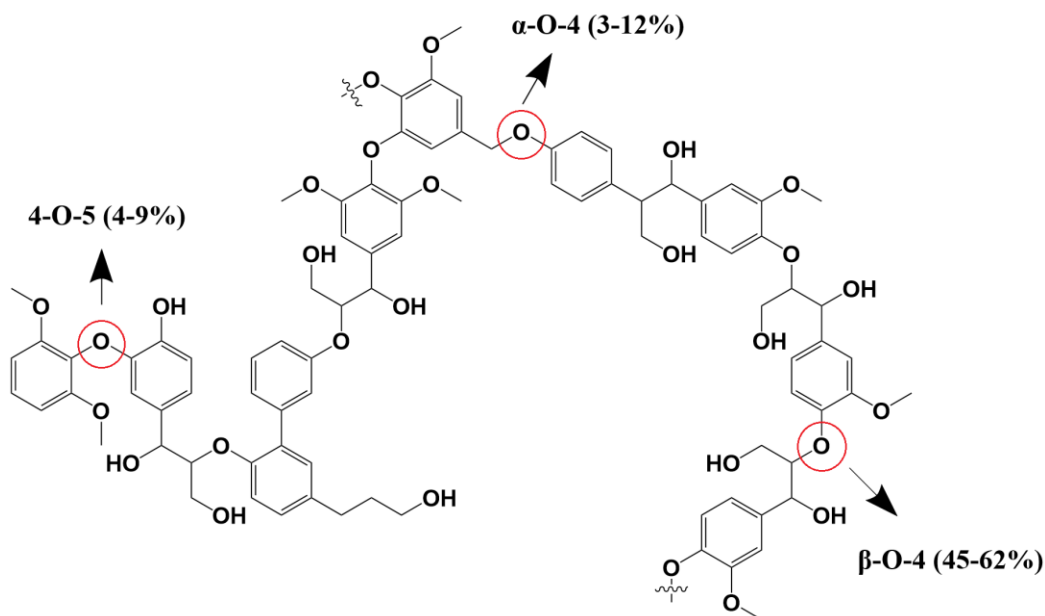


Fig. 1. The structure of three ether bonds in lignin

In the past decade, there has been a great deal of research on the high-value utilization of lignin. Thermochemical conversion is an important method, especially pyrolysis and gasification, which can be used to produce syngas or pyrolytic oil from lignocellulosic or lignin (Zhang *et al.* 2007; Bridgwater 2012; Ma *et al.* 2015). To date, lignin conversion has been studied from the perspectives of many scientific disciplines. New methods of enzymatic, mechanochemical, hydrothermal, electrochemical, and microwave-assisted lignin depolymerization have appeared. The field of chemical catalysis also has witnessed exciting progress (Chauhan 2020; Kausar *et al.* 2020; Gao *et al.* 2021; Nguyen *et al.* 2021; Roy *et al.* 2021). A large number of new catalysts have been applied to the pyrolysis of lignin and have been summarized in various excellent reviews (Sun *et al.* 2018). Although the depolymerization approach, which includes enzymatic and pyrolysis, can produce liquid products from lignin with platform monophenols for further

utilization, the product still shows poor thermal stability. This mainly arises from the high reactivity of lignin-derived phenolic intermediates, such as carbonyl groups. In order to stabilize reactive lignin-derived products to enhance their thermal stability, various hydrotreating methods have recently been proposed. Catalytic hydrotreatment is a capable way for lignin valorization that upgrades platform molecules by removing their oxygenated groups. It is used to cleave C–O–C and other oxygen containing linkages such as –OH and –OCH₃ in lignin and get more monophenols. Importantly, the depolymerization reaction of lignin requires selective cleavage of specific chemical bonds in lignin. This is the key to improving the yield of monophenol by hydrogenation of lignin.

Due to lignin's high energy density and intrinsic aromatic-based structure, it can be regarded as an ideal renewable feedstock that could be used in hydrogenolysis for the value-added chemicals. Currently, most of the lignin is burned directly for power production. Production of high-value chemicals (*e.g.*, phenols) from lignin is much more promising, and it will significantly enhance the economic competitiveness of biorefineries as well as support renewable energy goals. Although the use of hydrogen in industry is dangerous, current high-pressure equipment can be safely utilized in the presence of hydrogen. And research shows that hydrogen is only used to provide a reducing atmosphere during the reaction. At present, alcohol, acid or lignin itself can be used to replace hydrogen in the reaction system. It is expected that lignin can be converted into platform chemicals under safe and low-cost conditions by exploring and developing new and effective catalytic systems.

With the intensive research on lignin depolymerization, hydrogenation degradation of lignin has gradually become an important method for lignin depolymerization. In 1938, Harris and Adkins of the Chemistry Department at Wisconsin University first isolated carbohydrates from biomass by hydrogenation and degradation (Harris *et al.* 1938). In 1941, Freudenberg first studied the hydrogenation degradation of lignin and isolated isoeugenol, guaiacol, and cyclohexane products from lignin (Freudenberg and Lautsch 1939). Pepper and Hibbert in (1948) reported the degradation of maple lignin by hydrogenation under mild conditions and obtained monomeric products based on ethyl guaiacol and ethyl eugenol. In the 1950s, Pepper and Sakakibara's research group successively conducted a series of studies on the hydrogenation and degradation of lignin using hydrogen as hydrogen source (Sakakibara 1980). In 1986, Walter started to experiment with precious metals as catalysts for hydrogenation degradation reactions and achieved satisfactory results (Mycke and Michaelis 1986). With the development of technology and the increasing awareness of the dangers of hydrogen, Kirk and associates began to hydrogenate lignin by *in-situ* hydrogen supply in 2011 (Torr *et al.* 2011). At present, the hydrogenated degradation of lignin has become an accepted depolymerization method, and research on it has been increasing year by year.

After long-term study, it has been found that the hydrogenation degradation of lignin was affected by temperature, catalyst type, catalyst load, reaction time, solvent, and other factors. But so far, the hydrogenation degradation of lignin has not entered the industrial production stage, mainly because petrochemical products still occupy most of the market, and the cost of hydrogenation degradation is much higher than that of petrochemical products. Although the hydrogenation degradation of lignin has been studied for more than 80 years, the reaction mechanism and the reaction process are still not clear. The widely accepted conjecture is that hydrogenation begins with defibrillation of biomass and hydrolysis/solvolytic of lignin, which becomes fragmented and dissolved in organic solvents. Afterwards, the lignin fragments and products attach to the surface of

the catalyst and react with the free hydrogen atoms. Meanwhile, hydrogen molecules will dissociate on the surface of the catalyst and then diffuse into the reaction system to promote the degradation of lignin macromolecules. In this process, alkyl aryl ether bonds are selectively broken and reduced, and the lignin eventually forms stable monomers, dimers, and low molecular mass oligomers known as “bio-oils”. This paper presents an extensive review of the work on selective breaking of ether bonds in lignin. Therefore, the breaking behavior of the major ether bonds in lignin is presented in the next section. The product types and the distribution patterns of natural lignin in thermochemical reactions are then presented. The subsequent section describes the condensation reactions in the process of lignin pyrolysis and suggests means to mitigate the condensation reactions. Then the study of lignin pyrolysis pathway is reviewed, from the standpoints of two aspects: macro-kinetic modeling and molecular simulation of micro pyrolysis pathway. Finally, the prospect and challenges of lignin hydrogenation degradation are introduced.

HYDROGENATED DEGRADATION OF LIGNIN MODEL COMPOUNDS

Due to the complexity of lignin and the uncertainty of its three-dimensional structure, there are still huge differences in lignin structure between different materials and even different parts of the same material, so the macromolecular structure of lignin cannot be accurately described at present. To address this challenge and optimize subsequent studies, many scholars have opted to employ model compounds of lignin as the research objects. Lignin model compounds are not only an important tool for studying the structure of lignin, but they also provide a shortcut to study the reactivity of lignin. Combining experimental studies of well-defined model compounds with detailed kinetic calculations has proven to be a successful approach to understanding reaction mechanisms. However, lignin models need to be chosen carefully. If an overly simple model is selected, then the results obtained will not only fail to guide the subsequent experiments accurately, but also they can lead to completely wrong results. In the process of hydrogenation degradation of lignin to produce phenolic products, it is essential to use a hydrogen source to open the large number of ether bonds in lignin and to avoid the formation of carbon-carbon bonds as much as possible. Therefore, model compounds with different ether bonds should be selected in the hydrogenation degradation experiment of lignin model compounds. The following sections mainly discuss the three ether bond compounds with the highest content in lignin.

Hydrogenated Degradation of α -O-4 Ether Bond

There are three main ether bonds in lignin, namely α -O-4, β -O-4, and 4-O-5, with α -O-4 having the smallest bond dissociation energy of about 215 kJ/mol. In general, hardwood α -O-4 accounts for 3 to 12% of all aryl ether bonds, and the accuracy of this data remains in doubt (Gao *et al.* 2019). It has also been suggested that the α -O-4 ether bond accounts for only 0.3% of all bonds in lignin. Regardless of the accuracy of the data, it is certain that α -O-4 ether bond is a relatively important ether bond in lignin. During the fracture process, free radicals are easily formed and condensed again to form carbon-carbon bonds, and the newly formed products tend to be more stable and not easily degraded. Benzylidene aryl ether (BPE) generally has been selected as the model compound of α -O-4 in experiments. This is shown in Fig. 2.

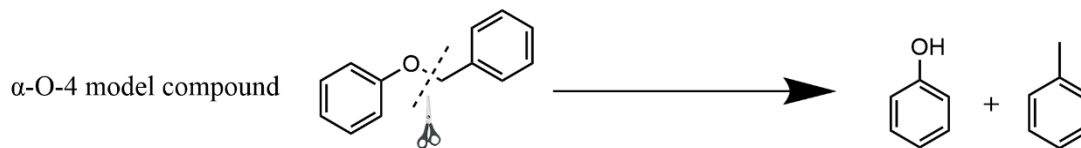


Fig. 2. Structure of α -O-4 model compound

Hartwig and associates (Sergeev and Hartwig 2011) designed a nickel-based homogeneous catalyst stabilized by N-heterocyclic carbene (NHC) ligand. The experimental results showed that the catalyst can efficiently break α -O-4 ether bonds at 80 to 120 °C. Under a hydrogen atmosphere of 1 bar, the conversion of the model compound was over 99%. Guaiacol and 4-methyl o-dimethyl ether were directionally generated by the reaction breaking of α -ether bond, and the yield of both products reached 99%. This reaction has a conversion rate and selectivity of 99% or more, depending on the special design of the catalyst. However, this reaction can only provide experimental design ideas for breaking α -O-4 ether bond, and it is difficult to achieve industrial production. This is mainly due to the complexity of the catalyst design and the fact that a homogeneous catalyst is difficult to recover.

Guan *et al.* (2020) compared the effects of external hydrogenation source and *in-situ* hydrogen supply on the reaction and found that the α -ether bond model 4-(benzyloxy) phenol (BOP) was catalyzed by the precious metal Pt-based catalyst Pt/HNbWO₆/CNTs. When the pressure to the reaction system reached 3 MPa, the conversion rate of α -O-4 model compound decreased from 98.1% in nitrogen atmosphere to 83.6% in hydrogen atmosphere. In this regard, the authors suggest that the difference is due to competition between hydrogen and reactants at the active site on the catalyst surface. Although the conversion rate of reactants decreases under hydrogen atmosphere, the comparison of the products formed in the two atmospheres shows that the monomer yield increases significantly, and the product types decrease under hydrogen atmosphere. This indicates that the hydrogen atmosphere can effectively stabilize the free radicals generated during the reaction and improve the selectivity of the product. In particular, the yield of the dimer product 4-benzyl-1,3-benzenediol decreased from 1.6% in the nitrogen atmosphere to 0% in the hydrogen atmosphere, indicating that the hydrogen atmosphere could inhibit the condensation of the product.

Metal-organic compounds have extremely high reactivity and product selectivity, but due to their complex preparation process, high cost, and the fact that most of them are homogeneous catalysts, they have high requirements on the subsequent catalyst recovery process and are not suitable for large-scale production and use. Precious metal catalysts also have shown excellent catalytic performance, as well as being easy to recycle and reuse. However, the cost of precious metal catalysts is too high, and they are extremely sensitive to sulfur, phosphorus, and other elements, which easily can poison and reduce the catalytic performance. In contrast, transition metals are good choice, as they also have excellent catalytic properties and are inexpensive and easy to recover, qualifying them as commercial catalysts. Song *et al.* (2020) using the transition metal Co/C@N as the catalyst and 20 bar hydrogen as the hydrogen source. They showed that the α -O-4 model compound can be completely transformed at 160 °C for 1 h. In addition, the yield of monomer toluene and cyclohexanol can reach 98.2%.

In order to avoid the potential dangers associated with high pressure hydrogen, Jiang *et al.* (2019) developed a supported metal Ni catalyst that also ameliorates the catalytic cost problems caused by noble metal catalysts. They prepared the Ni/Al₂O₃

catalyst and reacted in isopropyl alcohol at 130 °C for 3 h. The highest conversion of the reactants reached 58.9%, and the selectivity was as high as 100%. The substrate is completely converted to toluene and phenol.

In addition to using metal-organic, precious metals or transition metals as catalysts for hydrogenation degradation experiments, some scholars also have used metal salt solution for hydrogenation degradation lignin. Yokoyama *et al.* (1998) proposed that increasing the ionic content in the aqueous phase by adding salt not only facilitates the hydrolysis of the model species but also accelerates reactions such as hydrogen capture and free radical recombination. Inspired by this theory, Roberts *et al.* (2010) employed several different types of alkali metal carbonate solutions for catalytic hydrogenation of benzyl aryl ethers. The authors explored the effect of Li₂CO₃, Na₂CO₃, and K₂CO₃ on the reaction between 270 and 380 °C. They found that high selectivity of hydrogenation degradation could be achieved at low temperature and short reaction time, but at higher reaction intensity, the yield of phenol and benzyl alcohol would decrease, and large amounts of condensation products were formed.

Table 1 lists some investigations in which α -O-4 served as a model compound as the substrate for hydrogenation degradation reaction. The main reaction parameters are listed in the Table.

Table 1. Hydrogenation Degradation Reaction Conditions of α -O-4 Model Compounds

Catalyst	Reaction conditions				Conv. (%)	Selectivity (%)	Reference
	Temp. (°C)	Pressure	Time (h)	Solvent			
Ni-NHC	80	1 bar H ₂	16	Toluene	100	99	(Sergeev and Hartwig 2011)
TiN-Ni	125	12 bar H ₂	-	Ethanol	99	100	(Molinari <i>et al.</i> 2014)
Ni@SiC	90	6 bar H ₂	20	Water	99	99	(Zaheer <i>et al.</i> 2014)
Ni/Al ₂ O ₃	130	10 bar N ₂	3	Isopropanol	58.9	100	(Jiang <i>et al.</i> 2019)
Rh/Ni	95	2 MPa H ₂	17	Water	99	95	(Bulut <i>et al.</i> 2018)
Ru/Ni	95	1 MPa H ₂	16	Water	99	98	(Bulut <i>et al.</i> 2018)
Ni/AC	140	2 MPa H ₂	2	Methanol	100	88.5	(Zhu <i>et al.</i> 2019)
Raney Ni	80	N ₂	3	Propanediol	100	99	(Wang and Rinaldi 2012)
Pt/ CNTs	240	N ₂	3	Isopropanol	98.1	52.1	(Guan <i>et al.</i> 2020)
Pt/ CNTs	240	3 MPa H ₂	4	Isopropanol	83.6	88.3	(Guan <i>et al.</i> 2020)
Pd/Fe ₃ O ₄	240	10 bar N ₂	2	Isopropanol	100	100	(Paone <i>et al.</i> 2016)
PdFe/OMC	250	10 bar H ₂	1	Methanol	88.5	84	(Kim <i>et al.</i> 2015)
Ru/AC	120	N ₂	10	Isopropanol	99	98	(Wu <i>et al.</i> 2018)
Co/C@N	160	20 bar H ₂	1	Methanol	100	98.2	(Song <i>et al.</i> 2020)
B(C ₆ F ₅) ₃	30	N ₂	2	Dichloromet hane	100	60	(Feghali and Cantat 2014)
Carbonate	350	10 bar H ₂	1	Isopropanol	96	84	(Molinari <i>et al.</i> 2014)

Due to the fact that the α -O-4 ether bond is regarded as the weakest ether bond in lignin, it is easy to crack. According to the data in Table 1, it can be found that the model compounds can be completely transformed in most experiments in only a few hours, and the selectivity reaches more than 90%. Moreover, most catalytic systems only need the

hydrogenation of metal Ni, and do not need the loaded noble metal to provide stronger hydrogenation capacity. This is different from the catalytic systems for β -O-4 and 4-O-5 lignin model compounds.

Hydrogenated Degradation of β -O-4 Ether Bond

Among the three kinds of C-O ether bonds contained in lignin, the β -O-4 ether bond is the most important chemical bond in lignin structure. Its content can reach 46 to 60% of all the chemical bonds, and it is the main chemical bond broken during the degradation of lignin during pulping. The dissociation energy of β -O-4 ether bond is slightly higher than that of α -O-4 ether bond, about 289 kJ/mol (Gao *et al.* 2019). The fracture behavior of β -O-4 ether bond is closely related to the depolymerization route of lignin structure and the distribution of the products. In order to achieve the value-added utilization of lignin, many researchers have focused on the study of selectively breaking the β -O-4 ether bond. The structures of selected β -O-4 model compounds and their cleaved byproducts are shown in Fig. 3.

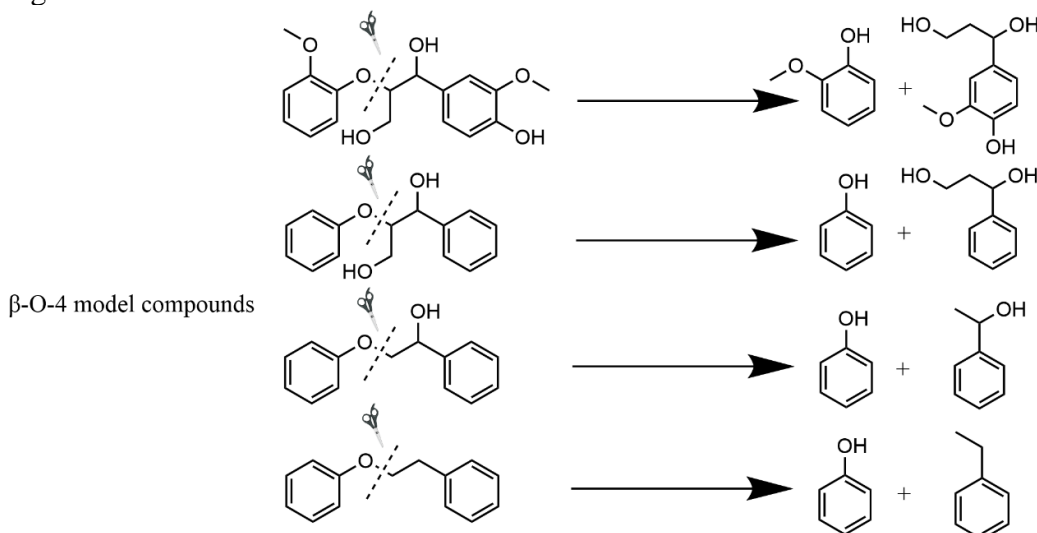


Fig. 3. Structure of β -O-4 model compound

Nichols *et al.* (2010) used a metal-organic catalyst to conduct directional depolymerization of the β -O-4 model compound 2-phenoxy-1-phenethanol and obtained excellent results. They designed a metallic ruthenium-based catalyst and were able to break the β -O-4 ether bond under milder reaction conditions and achieve more than 99% conversion and selectivity. Zhou *et al.* (2020a) also used 2-phenoxy-1-phenylethan-1-ol as the reaction substrate. They selected the lanthanum-nickel bimetallic catalyst (NiLa/CNT) supported on the carbon nanotube for catalytic hydrogenation reaction and finally obtained ethyl cyclohexane and cyclohexanol. The reaction was carried out with isopropyl alcohol as the solvent and H_2 as the hydrogen source for 4 h at 240 °C. The conversion of the substrate reached 100%, and the selectivity of ethyl-cyclohexane and cyclohexanol was 80% and 86%, respectively. This reaction was used for the first time to obtain cycloalkanes and cyclohexanols from a lignin model in one pot, which provides research direction and ideas for the preparation of jet fuel from biomass. Hossain *et al.* (2019) found that C α -OH in a lignin model compound can be used as a hydrogen source to supply hydrogen for hydrogenation reaction. They used 2-phenyl ethyl ether and 2-phenoxy-1-phenyl ethanol as reactants under Ru/C catalysis. They found that when the substrate was 2-phenyl ethyl

ether, the reaction did not occur, and no reaction products were detected. In contrast, when 2-phenoxy-1-phenyl ethanol was used as the substrate, the conversion of substrate could reach 52.5%, and the selectivity of phenol could reach 34.6%. This means that instead of relying on an external hydrogen source, the hydrogenolysis reaction can use the reactants themselves or the hydrogenolysis products to provide hydrogen source to drive the reaction continuously.

Although the above metal-organic catalysts have shown remarkable effects, their reaction substrates are still different from the lignin structural units. Natural lignin generally has phenolic hydroxyl groups, methoxy groups, and a complex side chain structure. Dou *et al.* (2020) compared two different lignin dimer model compounds and found that under the same hydrogenation conditions, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) propane-1,3-diol showed a significantly faster reaction rate than 2-phenoxy-1-phenylethanol. Under Co-Ni bimetallic catalysis, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) propane-1,3-diol reached 100% conversion of the substrate at 260 °C for 12 h, and the yield of main product guaiacol also reached 100%. In contrast, the conversion of 2-phenoxy-1-phenylethanol was 99.5% under the same reaction conditions, and the yield of the main product phenol was only 63%. This also means that the same β -O-4 model substance with different structures reacts at significantly different rates. Currently, the closest dimeric model to the natural lignin structure is guaiacylglycerol- β -guaiacyl ether, and according to the literature, the reaction rate of the model is even higher than 1-(3, 4-dimethoxyphenoxy)-2-(2-methoxyphenoxy) propane-1,3-diol (Li *et al.* 2020b). Parsell *et al.* (2013) adopted a bimetallic catalyst to catalyze the dimer, and the reaction conditions were relatively mild, and the yield of the reaction product could reach 85%. Some scholars have degraded guaiacylglycerol- β -guaiacyl ether to guaiacol as well as hibbertone by hydrolysis in a highly selective method. Jia *et al.* (2011) used ionic liquid as solvent and AlCl₃ as catalyst, and the reaction substrate guaiacylglycerol- β -guaiacyl ether was completely converted and 80% guaiacol was obtained after 120 min of reaction at 150 °C. This reaction provides an idea for the design of hydrogenated degradation reactions of natural lignin.

Inspired by the petroleum reforming reaction, He *et al.* (2012) used Ni/SiO₂ as a catalyst for hydrogenation degradation reaction. However, the results were not satisfactory. The β -O-4 model compound 2-phenylethyl phenyl ether reacts with 5 bar hydrogen at 120 °C for 90 min, and the conversion rate only reaches 20%, and the yield of the ethylbenzene is only 50%. Sturgeon *et al.* (2014) prepared a hydrotalcite-loaded metal Ni catalyst, which showed excellent catalytic performance in the hydrolysis of β -O-4 model compound. The reactants were reacted in methyl isobutyl ketone at 270 °C for 1 h. The conversion of the reactants could reach more than 90%, and the reaction products were phenol and acetophenone with the yields 95% and 85%, respectively. By comparing He's and Sturgeon's experiments, it is clear that metal Ni does have the ability to catalyze hydrogenation degradation reaction, but it is necessary to design catalyst support and reaction parameters to get ideal reaction results.

Table 2 lists some publications using β -O-4 model compound as the substrate for hydrogenation degradation reaction, and the main reaction parameters are listed in the table.

According to the data in Table 2, it can be found that the breaking of β -O-4 ether bond currently mainly depends on the hydrogenation of precious metals. Although the metal Ni also has superior hydrogenation characteristics, the hydrogenation effect is generally weaker than that of precious metals according to the current research. However,

the preparation of special supports and loading metal Ni is an effective method to replace precious metals, which is also the main research direction of lignin hydrocracking in the future. In addition, selecting hydrogen as a hydrogen source can significantly increase the conversion and selectivity of the reaction, but this operation not only has high risk factor, but also increases the cost of the whole reaction. It is a potential solution to use hydrogen supply solvent or product self-supplied hydrogen.

Table 2. Hydrogenation Degradation Reaction Conditions of β -O-4 Model Compounds

Catalyst	Reaction Conditions				Conv. (%)	Selectivity (%)	Reference
	Temp (°C)	Pressure	Time (h)	Solvent			
Ni/SiO ₂	120	5 bar H ₂	1.5	Water	20	50	(He <i>et al.</i> 2012)
Ni/HTC	270	N ₂	1	Methanol	90	98	(Sturgeon <i>et al.</i> 2014)
Ni/TiN	150	12 bar H ₂	-	Ethanol	99	100	(Molinari <i>et al.</i> 2014)
NiAu	130	10 bar H ₂	1	Water	100	57	(Zhang <i>et al.</i> 2014)
Ni/C	150	2 MPa H ₂	2	Methanol	99	85	(Song <i>et al.</i> 2013)
Ru-Phosphine	135	N ₂	1.75	Toluene	100	98	(Nichols <i>et al.</i> 2010)
ZnPd/C	150	2 MPa H ₂	2	Methanol	100	85	(Parsell <i>et al.</i> 2013)
Ru/NCM	260	1 MPa H ₂	3	Methanol	100	93	(Li <i>et al.</i> 2020)
Pd/C	80	N ₂	1	Ethanol	100	98	(Galkin <i>et al.</i> 2014)
Ru-Phosphine	135	1 MPa N ₂	20	Toluene	100	93	(Wu <i>et al.</i> 2012)
Pd/C	120	N ₂	16	m-xylene	100	93	(Gao <i>et al.</i> 2016b)
PdZn/C	150	3 MPa H ₂	8	Methanol	-	84	(Klein <i>et al.</i> 2016)
Pd/AC	240	0.1 MPa H ₂	2	Methanol	98.8	98.2	(Xie <i>et al.</i> 2019)
PdCl ₂	120	0.6 MPa H ₂	12	Methanol	99	98	(Cao <i>et al.</i> 2018)
Fe(acac) ₃	140	1MPa H ₂	24	Toluene	100	81	(Ren <i>et al.</i> 2013)
CoMo/Al ₂ O ₃	300	50 bar H ₂	4	Dodecane	100	30	(Jongerijs <i>et al.</i> 2013)
CuO-MgO/Al ₂ O ₃	150	25 bar H ₂	21	Ethyl acetate	99.1	24	(Strassberger <i>et al.</i> 2013)
HOTf	140	N ₂	2	Dioxane	100	99	(Deuss <i>et al.</i> 2015)

Hydrogenated Degradation of 4-O-5 Ether Bond

The idea of the presence of 4-O-5 ether bonds in the lignin unit was first proposed by Freudenberg and Chen (1967) due to their discovery that spruce produces a diphenyl ether structure after oxidation by potassium permanganate. Subsequent researchers isolated the same structure from Japanese larch and used 2D NMR to confirm the presence of 4-O-5 ether bonds. Among the three types of ether bonds of lignin, the 4-O-5 ether bond has the highest bond energy and is the least likely to break, with a dissociation energy of about 314 kJ/mol (Bulut *et al.* 2018). Therefore, it is often necessary to increase the reaction temperature or pressurize the reaction system appropriately during hydrogenated degradation to achieve selective breaking of the 4-O-5 ether bonds. The structure of the 4-O-5 model compound is shown in Fig. 4.

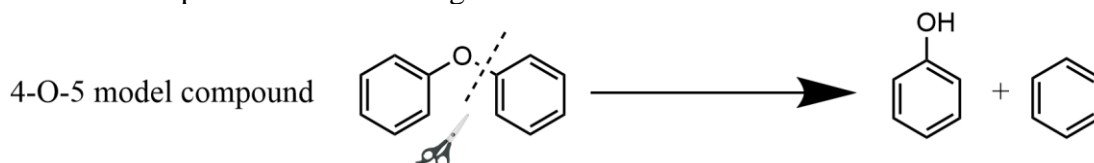


Fig. 4. Structure of 4-O-5 model compound

Ren *et al.* (2013) used $\text{Fe}(\text{acac})_3$ as catalyst for hydrogenation of 4-O-5 model compound diphenyl ether and showed interesting results. When the authors used LiAlH_4 as reducing agent, the reaction substrate was completely transformed into phenol and benzene. Since LiAlH_4 is more dangerous and can explode on contact with water, when LiAlH_4 was replaced with 5 MPa hydrogen, the reaction under the same conditions but the presence of phenol and benzene was almost undetectable. Jin *et al.* (2015) found that the hydrolysis path of diphenyl ethers was different under different H_2 pressures. Under high hydrogen pressure, diphenyl ethers undergo the first aromatic ring hydrogenation saturation reaction, followed by metal-catalyzed or acid-catalyzed C-O ether bond cleavage reaction, finally forming cyclohexane and cyclohexanol. At low hydrogen pressure, direct cleavage of the 4-O-5 ether bond first occurs to form benzene and phenol, and phenol will continue to hydrogenate to form cyclohexane. This means that it is possible to regulate the hydrogenolysis products of the 4-O-5 ether bond model by controlling the hydrogen pressure during the reaction. By comparing the metal Ni catalytic hydrogenolysis reactions of three model species, α -O-4, β -O-4, and 4-O-5, He *et al.* (2012) found that the fracture mode of ether bond of 4-O-5 was completely different from that of the other two modes. The 4-O-5 ether bond model will become hydrogenated to form cyclohexyl phenyl ether when the ether bond is broken by hydrogen dissociation. This intermediate product will be further hydrogenated to form cyclohexane and phenol.

Zeng *et al.* (2018) reported a route for the highly selective conversion of biphenyl ethers to amine derivatives catalyzed with metallic palladium catalyst, and the synthesized amine derivatives can be used as important components in pharmaceuticals, fine chemicals, and electronic materials. The authors found that the conversion of biphenyl ethers could reach 99% when NaBH_4 was selected as the hydrogen source, and the yield of the product 1-cyclohexyl-1H-pyrrole could reach 77%. They also found that when the hydrogen source used in the experiment was replaced with hydrogen, the hydrogenation efficiency decreased, and the product yield was only 68%.

Table 3 shows a summary of experiments on hydrogenated degradation of lignin 4-O-5 ether bond model species in recent years. Since the 4-O-5 ether bond is the least likely to break among the three types of ether bonds, the reaction conditions required are the most

demanding. Moreover, under relatively intense reaction conditions, hydrogenation cleavage and hydrodeoxygenation begin to occur simultaneously. Therefore, most of the products of these reactions have the presence of cyclohexane or cyclohexanol.

Table 3. Hydrogenation Degradation Reaction Conditions of 4-O-5 Model Compounds

Catalyst	Reaction Conditions				Conv. (%)	Selectivity (%)	Reference
	Temp. (°C)	Pressure	Time (h)	Solvent			
Ni-NHC	120	1 bar H ₂	16	Butanol	99	99	(Sergeev and Hartwig 2011)
Ni/SiC	120	6 bar H ₂	20	Water	96	97	(Zaheer <i>et al.</i> 2014)
Raney Ni	140	N ₂	4	n-hexadecane	99	87	(Spasyuk <i>et al.</i> 2013)
TiN-Ni	150	12 bar H ₂	-	Ethanol	99	95	(Molinari <i>et al.</i> 2014)
Ni/C	180	1 bar H ₂	24	Butanol	99	99	(Gao <i>et al.</i> 2016a)
Ni/Al ₂ O ₃	150	10 bar N ₂	-	Isopropanol	99	75	(Jiang <i>et al.</i> 2019)
Pd/Ni	240	1 MPa N ₂	1.5	Isopropanol	96	91	(Mauriello <i>et al.</i> 2018)
Pd/Ni	10	1 MPa H ₂	1.5	Isopropanol	73	96	(Mauriello <i>et al.</i> 2018)
Ni(acac) ₂	70	N ₂	5	Toluene	60	99	(Samant and Kabalka 2012)
PdAu/Ce O ₂	180	N ₂	24	-	100	90	(Gao <i>et al.</i> 2019)
RuWO/Si Al	270	2.2 MPa H ₂	3	Water	100	-	(Huang <i>et al.</i> 2015)
Ru/C	120	N ₂	10	Isopropanol	99	50	(Wu <i>et al.</i> 2018)
RuNi/AC-N	230	1 MPa H ₂	4	Water	98	58	(Hu <i>et al.</i> 2018)
Rh/C	80	10 MPa CO ₂	5	Water	100	96	(Chatterjee <i>et al.</i> 2013)
Fe(acac) ₃	140	N ₂	24	Butanol	81	97	(Ren <i>et al.</i> 2013)

HYDROGENATED DEGRADATION OF NATURAL LIGNIN

Hydrogenated degradation is a promising method for lignin depolymerization because the yield of monomeric products obtained by hydrogenolysis is usually higher and the products tend to be simpler than those produced by other degradation methods. Extensive research in the 1980s and earlier led to the development of several processes for the production of monophenols from liginosulfonate and kraft lignin. There are several ways to achieve hydrogenated degradation of natural lignin. For raw materials, wood chips can be directly hydrogenated without removing cellulose and hemicellulose. In this way, the yield of fatty alcohol may be increased. Secondly, the process can hydrogenate degradation compounds of lignin produced by the pulp and paper industry or waste lignin

from the bioethanol industry. As the lignin is treated in various ways during the treatment process, the ether bond content in the lignin is reduced and cannot be easily degraded by hydrogenation, resulting in a lower yield of hydrolysis products. For the hydrogenated degradation method, the lignin can be degraded directly, *i.e.*, by means of a one-pot method, which is convenient and low-cost for industrial production, but the product yield is low. Secondly, before hydrogenation and degradation, a pretreatment step is taken to activate the lignin first, which is conducive to the subsequent degradation step. The yield of products obtained in this way is slightly increased, but the cost will inevitably increase. For the hydrogen supply method, hydrogen can be supplied by direct reaction with hydrogen, which requires milder reaction conditions but is more costly and dangerous to operate. Secondly, solvents can be used to supply hydrogen to the reaction. For example, alcohols, acids, and other solvents can be used as hydrogen supply solvents at high temperatures to provide hydrogen ions. Inspired by the solvent-supplied hydrogen, some scholars have recently tried to supply hydrogen by lignin for the reaction. Alcohol monomers obtained from the degradation of lignin can provide a reducing atmosphere for the subsequent reaction, which is a relatively potential method of hydrogenation degradation.

Hydrogenated Degradation Using Hydrogen Molecules to Supply Hydrogen

Hydrogenation degradation usually requires the hydrogen sources to promote the rapid reaction of the reactants, and among the many types of hydrogen sources, hydrogen itself is the most widely used. Hydrogen has superior hydrogenation ability, which can promote the reaction and stabilize the intermediate free radicals generated in the reaction process. This property makes the hydrogenation degradation products less diverse and convenient for subsequent separation and utilization.

Torr *et al.* (2011) performed hydrogenation degradation experiments on three different treatments of the raw materials (radiata pine after extraction, radiata pine after steam explosion, and radiata pine Enzymatic Mild Acidolysis Lignin (EMAL)) by means of external hydrogen supply. The reaction was charged with 3.45 MPa H₂ for 24 h at 195 °C. The results showed that the conversion of radiata pine EMAL lignin reached 89% at the end of the reaction, while the conversion of radiata pine after extraction was only 79%. The hydrogenation degradation products of both were dominated by dihydroconiferyl alcohol and 4-n-propyl guaiacol, and the yield of the two hydrolyzed products were 19 to 21% and 2%, respectively. This means that the presence of carbohydrates in radiata pine affects the removal rate of lignin macromolecules, but not the hydrogenation degradation rate of lignin. Compared with the above two raw materials, the quality conversion and product yield of radiata pine treated by steam explosion were extremely low. This is attributed to the massive disruption of the β -O-4 ether bond during the steam explosion and the condensation reaction. This result may provide a research direction for the hydrogenation degradation of lignin, which requires the selection of raw materials with high content of β -O-4 ether bond as substrates to maximize the yield of monomer products.

Although the above processes have shown that the hydrogenation activity of lignin will be reduced after chemical reaction or treatment, the main source of lignin at present is the black liquor produced by pulp and paper factories. In order to investigate the hydrogenation activity of alkali lignin, Tran *et al.* (2021) used commercial alkali lignin for hydrogenation degradation experiment. They designed and prepared catalyst Cu@MIL-101(Cr), and optimized the reaction temperature, catalyst load and substrate concentration in the reaction. It was found that under the optimal reaction conditions, the conversion of

alkali lignin could reach 57%, and the yield of monomer product was 38.5%. Zhang *et al.* (2021) also conducted hydrogenation degradation experiment on commercial alkali lignin, and the author prepared hydroxyapatite supported noble metal Pt catalyst. Through the synergistic effect between the acid site and the metal site, the yield of phenolic monomer reached 15.1%.

Due to the mild extraction process, the treatment severity of organic solvent lignin is generally between EMAL and alkali lignin; therefore, the β -O-4 ether bond content in organic solvent lignin should likewise be between EMAL and AL. Research has shown that organic solvent lignin retains the original ether bond of lignin. Zhang *et al.* (2014) prepared an Au-Ni core-shell catalyst to achieve mild hydrogenated degradation of organic solvent lignin. The reactor was charged with 1 MPa H₂, and the reaction was conducted at 170 °C for 12 h. The yield of phenolic monomers could reach 14%. This catalyst significantly reduced the reaction temperature of hydrogenated degradation process. Xu *et al.* (2021b) prepared a highly dispersive Ni/Al-SBA-15 catalyst and used it in the hydrogenated degradation experiment of solvent lignin. The reactor was charged with 1 MPa H₂, and the reaction was conducted at 280 °C for 2 h. The yield of phenolic monomers could reach 21.36%. The experimental results showed that the catalyst can effectively inhibit the formation of coke during the reaction.

Renders *et al.* (2016a) used poplar wood as a raw material for the hydrogenated degradation by a one-pot method, where the authors used a Pd/C catalyst and the reaction product was divided into two parts. The liquid phase products were mainly lignin monomer compounds, while the solid phase product was mainly cellulose, which can be used for the subsequent preparation of cellulose products. A mixture of methanol and water was used as the solvent during the reaction, allowing the small lignin molecules depolymerized by the reaction to be dissolved and recovered. When poplar reacted with hydrogen pressure of 20 bar at 200 °C for 3 h, the lignin monomer products mainly included 4-propyl eugenol 4.4%, 4-propyl guaiacol 0.6%, 4-propanol eugenol 21.5%, 4-propanol guaiacol 14%, and the total monomer yield of the product was 43.5%. Moreover, the authors found that the carbohydrate yield could be adjusted by adjusting the ratio of water to alcohol. When the ratio of water is relatively low, a large amount of carbohydrates will be retained, while when the ratio of water is more than 70%, hemicellulose will become hydrolyzed, resulting in reduced carbohydrate yield. Gong *et al.* (2021) chose a transition metal catalyst MoO₂/C to carry out hydrogenated degradation of miscanthus with a reaction pressure of 3 MPa H₂ and at 240 °C for 4 h. The main products of hydrogenation degradation were *p*-coumaric acid ethyl ester and ferulic acid ester, and the yields were 8.7% and 6.4%, respectively. Secondly, the products also included 4-propylene guaiacol, eugenol, and other phenolic products, and the yield of total monomer reached 26.4%. In addition, the carbohydrate was well retained after treatment, and glucose and xylose were easily obtained by enzymolysis, thus realizing the efficient utilization of the three components of herbaceous biomass.

Hydrogenated Degradation by Solvent Supply Hydrogen

The hydrogenation reaction can occur without relying on hydrogen but using some solvent as a hydrogen donor. In the subcritical or supercritical state, alcohols, acids, and water have been shown to act as hydrogen donors and also as solvents for reactions. This strategy not only reduces the risk of reaction process, but also greatly reduces the cost of reaction. Such solvents, working together with suitable catalysts, can provide the necessary hydrogen for the breaking of ether bonds in lignin macromolecules. Therefore, it is

important to select the appropriate solvent and catalyst in the hydrogenation degradation of lignin.

Cheng *et al.* (2021) used poplar organosolv lignin (treated with methanol/water) as feedstock for hydrogenation degradation, using bimetallic Ni-Cu/C as catalyst. The authors suggested that the addition of Cu in the catalyst promoted the hydrogen supply process and reduced the amount of ethanol/isopropanol. Furthermore, Two-dimensional Heteronuclear Single Quantum Coherence Nuclear Magnetic Resonance (2D HSQC NMR) and The Matrix-Assisted Laser Desorption Ionization-Time of Flight Mass Spectrometry (MALDI-TOF MS) analyses showed that the metal Cu further promoted the cleavage of lignin bonds, especially the coniferyl-type structure. The results showed that 63.4% of the monomer phenols were hydrogenated and degraded under the nitrogen pressure of 1 MPa and 270 °C for 4 h. Hu *et al.* (2020) used isopropanol as the hydrogen source and NiPd/SBA-15 as the catalyst for the hydrogenated degradation of softwood (pine), hardwood (birch), and herbaceous (corn straw) biomass. When the three raw materials reacted at 250 °C for 4 h, the yield of birch monomer was the highest, reaching 37.2%. Compared with birch, pine and corn straw, the monomer yield was 16.9% and 8.1%, respectively. This means that hardwood is more susceptible to hydrogenated degradation reactions than other wood species. Su *et al.* (2022) also hydrogenated degradation three types of 10 different materials, and finally found that the monomer yield of hardwood species was significantly higher than that of softwood and herbaceous.

Since the main products of lignin in the degradation process are phenols, in order to investigate the influence of phenolic products on the hydrogenation degradation reaction, Zhou *et al.* (2018) used ethanol-phenol as the hydrogen solvent to conduct the hydrogenation degradation experiment of alkali lignin. They found that the proper addition of phenol helped further depolymerization of lignin to obtain more bio-oil and reduce the yield of solid residue. However, excessive phenol would condense with the reaction intermediates, leading to a decrease in the yield of bio-oil. The authors indicated that the optimal ratio of phenol/lignin was 0.8. Under this condition, the yield of bio-oil could reach 81.8% by using CuNiAl as catalyst at 290 °C for 3 h.

Acid solvents are also excellent hydrogen donor solvents. For example, Lu *et al.* (2022) used formic acid/isopropanol as a hydrogen donor solvent and tried MCM-41 as a catalyst to catalyze the hydrogenated degradation of lignin. They found that the addition of metal Al enhances the surface acidity of the catalyst, while Ni and Mo can synergistically enhance the reduction of the catalyst. Therefore, NiMoAl/MCM-41 catalyst was prepared and used for hydrogenated degradation of lignin. After the reaction at 240 °C for 8 h, the lignin conversion rate was 76% and the yield of bio-oil was 61.6%. Oregui-Bengoechea *et al.* (2017) revealed the role of formic acid in hydrogenated degradation reaction through experiments. By replacing formic acid in solvent with H₂ and isopropanol, the authors found that the yield of bio-oil was significantly different. In contrast, they found that the yield of bio-oil obtained from H₂ and isopropanol as hydrogen sources were similar. Therefore, the role of formic acid in the reaction was not only the hydrogen donor, but also participated in the reaction, stabilizing the intermediate of hydrogenation process, improving the yield of bio-oil and reducing the coke content.

In order to further reduce the cost of the experiment and the pollution of the experimental process, Wang *et al.* (2018) used water as the hydrogen supply solvent for *in-situ* hydrogenation degradation of poplar organosolv lignin (treated with 1,4-dioxane). They used NiAl alloy as a catalyst for the hydrogenation reaction. In an alkaline aqueous solution, the Al atoms are corroded to expose the internal Ni layer, while the corrosion

process generates hydrogen. The generated hydrogen is easily contacted with the active site of Ni, which enables the hydrogenation degradation process of lignin. The results showed that the conversion of lignin could reach 86.8%, and the monomer yield could reach 18.9%. Fan *et al.* (2021) compared the effects of three kinds of composite solvents of water and alcohol (methanol, ethanol, and isopropyl alcohol) on hydrogenation degradation. It was found that birch was more easily degraded into monomer phenols in the composite solvent of methanol and water, and the monomer yield reached 28.5% at 190 °C for 3 h. In addition, the solid residue retained 92% of the cellulose and 57.3% of the hemicellulose, which can be further used in the pulp and paper industry or for the preparation of bioethanol.

Hydrogenated Degradation by Lignin Self-supply Hydrogen

Either using an external hydrogen source or using solvent to supply hydrogen to the reaction will increase the cost of the process, which is unfavorable to large-scale production. Recently, self-hydrogen transfer hydrogenolysis using the hydroxyl group of lignin as hydrogen donor has become a promising method for hydrogen-free depolymerization.

Luo *et al.* (2017) developed a strategy using C α H-OH, an intermediate product of hydrogen hydrolysis, as a hydrogen donor. They designed a photocatalytic assisted hydrogenation degradation experiment in which ZnIn₂S₄ was used as a catalyst to inhibit the conversion of phenolic products to quinones products under visible light irradiation at low temperatures (below 50 °C). With this strategy, the yield of lignin β -O-4 model compound was 71 to 91%. Although the monomer yield is not as high as when using an external hydrogen supply or solvent supply, this method of hydrogen supply is a highly promising strategy. Zhang *et al.* (2017) prepared MIL-100(Fe) supported Pd-Ni metal-organic framework catalyst and used it for hydrogen dissolving polymerization of lignin model. They found that the catalyst could use lignin itself as a hydrogen source to hydrogenate lignin, and the catalytic effect did not decrease significantly after the catalyst was reused five times. Xu *et al.* (2021a) prepared a photocatalytic degradation catalyst by combining Zn₄In₂S₇ with graphene oxide. They found that the lignin itself was a hydrogen supplier, and the conversion of the lignin model compound reached 93.27%.

Due to the low content of β -O-4 ether bond in industrial lignin, the depolymerization of phenol products was insufficient, and the self-hydrogen transfer hydrogen depolymerization was mostly carried out by lignin model compounds. Dou *et al.* (2022) used natural lignin for hydrolysis and found that C α -OH in lignin macromolecules dehydrogenated on the surface of catalyst Pd-PdO/TiO₂ and would become the hydrogen source for subsequent hydrolysis. The authors compared four different materials (pine, willow, sorghum, and poplar), and finally the poplar lignin monomer yield was the highest, which could reach 40%.

Most of the above hydrogenation degradation reactions are “one-pot methods” without pretreatment of lignin. Such methods are simple and convenient, but the product yields are not high, and the product selectivity is low. Kärkäs (2017) used TEMPO oxidation to activate oxygen-containing functional groups in lignin before the hydrogenation degradation process, which improved the reaction performance of lignin. At the same time, the author added formaldehyde to the reaction system as the end sealing agent to avoid the recondensation of degraded lignin molecules. The author obtained monomer yields of up to 78 % with formaldehyde as a stabilizing agent after being subjected to hydrogenolysis with Ru/C at 250 °C for 15 h. In contrast, the absence of

formaldehyde gave a monomer yield of only 24 %. This strategy can overcome the problem of lignin condensation in the traditional one-step method.

The hydrogenated degradation reactions of natural lignin that have been carried out in recent years are listed in Table 4. As can be seen from the table, the lignin prepared with organic solvent generally has higher reactivity and monomer yield because it retains a large number of active functional groups. Secondly, because the wood powder has not undergone chemical reaction, the ratio of carbon-carbon bond is low, so the yield of monomer obtained by hydrogenation degradation is also high. However, during the pulping process, a large number of chemical reactions occur, leading to a large number of condensation reactions between lignin molecules, so the hydrogenation degradation efficiency of alkali lignin is low, which is the biggest problem in the current high-value utilization of alkali lignin.

Table 4. Hydrogenation Degradation Reaction Conditions of Natural Lignin

Material	Catalyst	Reaction Conditions				Monomer Yield (%)	Reference
		Temp. (°C)	Pressure	Time (h)	Solvent		
Maple	Raney Ni	173	210 bar H ₂	6	Dioxane	27.3	(Brewer <i>et al.</i> 1948)
Poplar	Raney Ni	220	35 bar H ₂	5	Dioxane	59.1	(Pepper & Steck 1963)
Poplar	Rh/C	195	34 bar H ₂	5	Dioxane	50.1	(Pepper & Supathna 1978)
Birch	Pt/C	200	40 bar H ₂	4	Dioxane	46.5	(Yan <i>et al.</i> 2008)
Pine	Pd/C	195	34.5 bar H ₂	24	Dioxane	22.4	(Torr <i>et al.</i> 2011)
Birch	Ru/C	250	30 bar H ₂	6	Methanol	51.5	(Van den Bosch <i>et al.</i> 2015b)
Poplar	Zn-Pd/C	225	34.5 bar H ₂	12	Methanol	54	(Parsell <i>et al.</i> 2015)
Birch	Pd/C	250	30 bar H ₂	3	Methanol	49.3	(Van den Bosch <i>et al.</i> 2015a)
Poplar	Pd/C	200	20 bar H ₂	3	Methanol	42	(Renders <i>et al.</i> 2016b)
Miscanthus	Ni/C	225	60 bar H ₂	12	Methanol	68	(Luo <i>et al.</i> 2016)
Beech	Ni/C	200	60 bar H ₂	5	Methanol	51.4	(Chen <i>et al.</i> 2016)
Poplar	Pd/C	200	20 bar H ₂	3	Methanol	43.5	(Renders <i>et al.</i> 2016a)
Poplar	Pd/C	200	20 bar H ₂	3	Ethanol	43.3	(Renders <i>et al.</i> 2016a)
Birch	Pd/C	200	30 bar H ₂	3	Water	43.8	(Schutyser <i>et al.</i> 2015)
Cornst alk	Al(OTF) ₃	200	30 bar H ₂	3	Methanol	24.5	(Anderson <i>et al.</i> 2016)
Birch	Pd/C	180	30 bar H ₂	2	Methanol	55	(Huang <i>et al.</i> 2017a)
Oak	Pd/C	180	30 bar H ₂	2	Methanol	46	(Huang <i>et al.</i> 2017b)
Birch	NiFe/C	200	20 bar H ₂	6	Methanol	39.5	(Zhai <i>et al.</i> 2017)
Birch	Ni/Al ₂ O ₃	250	30 bar H ₂	3	Methanol	36	(Van den Bosch <i>et al.</i> 2017)
Birch	Pd/C	180	30 bar H ₂	3	Methanol	37	(Kumaniaev <i>et al.</i> 2017)
Alkali lignin	Pt/HAP	250	3 MPa H ₂	20	Ethanol	15.1	(Zhang <i>et al.</i> 2021)
Alkali	Ir/HAP	250	3 MPa H ₂	20	Ethanol	14.6	(Zhang <i>et al.</i> 2021)

lignin							
Alkali lignin	Rh/HAP	250	3 MPa H ₂	20	Ethanol	13.2	(Zhang <i>et al.</i> 2021)
Alkali lignin	Ni/HAP	250	3 MPa H ₂	20	Ethanol	12.3	(Zhang <i>et al.</i> 2021)
Alkali lignin	Ru/HAP	250	3 MPa H ₂	20	Ethanol	11.4	(Zhang <i>et al.</i> 2021)
Solvlig nin	Ni-ZrP	270	3 MPa H ₂	4	isopropa nol	14.6	(Ma <i>et al.</i> 2019)
Birch	Ni/C	200	2 bar N ₂	6	Methanol	32	(Klein <i>et al.</i> 2015)
Pine	Sulf-Acid	170	N ₂	0.1	Methanol	10	(Kaiho <i>et al.</i> 2015)
Birch	Pd/C	210	Ar	15	Ethanol	36	(Galkin <i>et al.</i> 2016)
Solvlig nin	NiCu/C	270	1 MPa N ₂	4	isopropa nol	63.4	(Cheng <i>et al.</i> 2021)
Acid lignin	PtRe/TiO ₂	240	He	12	isopropa nol	18.71	(Hu <i>et al.</i> 2019)
Lignin residue	Ru/C	300	20 bar N ₂	3	isopropa nol	22.43	(Kim <i>et al.</i> 2017)
Alkali lignin	Ni/SBA	100	Air	0.5	Formic acid	38	(Toledano <i>et al.</i> 2013)

INHIBITION OF LIGNIN CONDENSATION DURING DEGRADATION

In lignin hydrogenated degradation experiments, lignin macromolecules undergo homolytic reactions at high temperature and pressure, leading to the production of intermediate products with free radicals. These intermediate products are extremely unstable. They can easily condense with each other to form carbon-carbon bonds. Such condensation is undesirable in the hydrogenated degradation reaction, because what is formed after condensation is often a carbon-carbon bond that is more difficult to break, so that not only the monomer yield will decrease, but also a large amount of coke will be formed. The most easily broken chemical bond during hydrogenated degradation is the β -O-4 ether bond. When the β -O-4 ether bond content in natural lignin or lignin obtained by pretreatment is higher, the lignin monomer content is also higher (Schutyser *et al.* 2018). However, lignin macromolecules contain not only β -O-4 ether bonds, but also a large number of carbon-carbon bonds, which leads to incomplete lignin cleavage and the monomer yield is decreased. Li *et al.* (2023) reported a catechol lignin that is 100% catechol units in the lignin macromolecule due to the lack of O-methyltransferase (OMT). This lack prevents the conversion of lignin from catechol to guaiacol, which resulted in the absence of carbon-carbon bonds in this lignin. By hydrogenated degradation of this lignin, they found that the monomer products yield could reach 90%.

Shuai and Saha (2017) found that the condensation and degradation of lignin were two parallel reactions, both affected by reaction temperature and time. Therefore, simply optimizing these parameters could not fundamentally solve the condensation phenomenon. They found that the main reason for lignin condensation is the reaction of formaldehyde with α -C to form C α -OH, which further reacts to form methylene quinone structure, which is the positive center on the benzene ring and directly participates in the condensation reaction. In this regard, there are two solutions. The first is to add a formaldehyde-trapping agent. The addition of phenolic substances can reduce the concentration of formaldehyde and improve the yield of biological oil in the reaction process. The other solution is to add

excessive formaldehyde to the reaction system, so that formaldehyde can completely consume the reaction sites on the benzene rings, making it impossible for lignin to react from C α -OH to form methylene quinone structures. According to the above theories, Shuai *et al.* (2016) inhibited the formation of carbon-carbon bonds by adding formaldehyde in the reaction and obtained effective results. They found that the monomer yield was only 7 to 26% without formaldehyde, while the monomer yield reached 47 to 78% after formaldehyde was added. The cited authors also reduced the depolymerization path of the lignin model by analyzing the degradation products. They proposed the mechanism of formaldehyde inhibiting the formation of carbon-carbon bonds, suggesting that the main mechanism is to protect the highly active hydroxyl sites through the condensation reaction of aldehydes. The degradation products will not react during the degradation process, thus reducing the formation of oligomers. Lan *et al.* (2018) compared a variety of aldehydes, including formaldehyde, and alcohols to investigate their effects on the yield of monomer products. They found that, except for 5-hydroxymethylfurfural, other aldehydes had a promoting effect on the yield of monomers, and the promoting effect of acetaldehyde and propionaldehyde was comparable to that of formaldehyde, which was the highest among all reagents. In addition, ketone structures such as acetone and butanone, as well as alcohols also contribute to the increase of lignin monomer yield.

Inspired by the above experiments, the α -position hydroxyl group tends to activate the β -aryl ether bond by oxidizing to a carbonyl group during the experimental process of hydrogenated degradation, leading to the breakage of the β -ether bond. The generated monomer is easily condensed with other monomers to form coke due to the presence of reactive groups such as carbonyl groups. Therefore, by adding alcohols to the solution, according to the principle of aldol reaction, the alcohols can combine with the active carbonyl group to form an acetal structure to protect the carbonyl group and reduce the formation of condensation products during the reaction. Deuss *et al.* (2017) found that the formation of oligomers could indeed be reduced by adding ethanediol to the reaction solution in order to achieve aldol condensation with the carbonyl group in the reaction product.

Schutyser *et al.* (2018) suggested that lignin condensation could be prevented in the following ways: Reacts with lignin under mild conditions through ammonia-based strategies; Formaldehyde was added to the reaction system to protect β -O-4 from destruction; Physically remove the reaction intermediates from the heating zone; Hydrogen is used to reduce the reaction intermediate to a stable product. Based on the above views, we made several suggestions for the inhibition of polymerization of monomers during the hydrogenated degradation of lignin.

a) The reaction should be carried out under mild reaction conditions such that the resulting products are not easily polymerized, as in the case of enzymatic lignin. However, this method requires a long time, and the biological enzymes are more demanding on the environment;

b) The reaction can take place in some specific solvents, such as ammonia solutions, ionic liquids, *etc.* Although the lignin obtained in this way is effective and active, liquid ammonia as well as ionic liquids are more expensive to prepare and not easily recyclable;

c) It is recommended to add stabilizers, which are currently known to include formaldehyde (to form stable ketone products), alcohols, *etc.* This approach is relatively convenient, but also requires the presence of specific side chain functional groups in the lignin to achieve it;

d) Carry out the reaction under reductive conditions. Generally, the reaction is carried out in the atmosphere of hydrogen, which is costly and dangerous;

e) Employ physical methods, where the product after the reaction is moved out of the reaction system in time. This approach reduces coke formation and facilitates positive reaction progress, but it requires a large amount of gaseous or liquid mobile phase, resulting in dilution of the product as well as high solvent usage and increased energy consumption for subsequent separation.

MECHANISM OF LIGNIN HYDROGENATED DEGRADATION

The unique three-dimensional structure of lignin has stood in the way of clearly determining the depolymerization process. This problem also has prompted more and more scholars to explore the mechanism of lignin depolymerization, which is essential for the targeted depolymerization of lignin macromolecules, preparation of high-value chemical platform compounds and design of efficient catalysts. However, due to the variety of lignin, the study of the depolymerization mechanism is still a major challenge so far. Generally speaking, there are two ways to investigate the mechanism. One is to perform theoretical calculations through density functional theory. By calculating the activation energy of each step in the reaction process, it is thus possible to figure out the most likely reaction path (Li *et al.* 2020b). The other approach is to track the reaction steps of the reaction by labeling the atoms in the model with isotopes (Zhou *et al.* 2020b). Both methods have their own characteristics, but both are limited to lignin model compounds.

Lu *et al.* (2016) chose 2-phenoxy-1-phenylethanol as the lignin model compound, combined with density functional theory calculation and the experimental study on the C-O ether bond in the pyrolysis mechanism of Pd catalyst. According to the calculation, the optimal reaction mechanism is as follows: 2-Phenoxy-1-phenylethanol is dehydrogenated at the α -carbon and then at the -OH group to produce the corresponding ketone: 2-phenoxy-1-phenylethanone. The ketone interconverts isomerically to 2-phenoxy-1-phenylvinyl alcohol, forming the enol form, which then dehydrogenates at the -OH group and subsequently cleaves the C-O ether bond. The authors concluded that direct C-O ether bond cleavage of the reactants is unlikely to occur over the Pd catalyst and must be preceded by reactant dehydrogenation process. The hydrogen atoms on the α -C and β -C are essential for the reaction to proceed.

Li *et al.* (2020b) explored the mechanism of ether bond breaking using a 4-O-5 lignin model compound in combination with density functional theory (DFT). They concluded that hydrogenolysis reaction mechanisms begin with dissociative adsorption of H₂ onto the palladium catalyst surface, generating surface-bound hydrogen atoms. The Pd-H species of the catalyst will react with the C₅-C₆ bond of the benzene ring and adsorb to the benzene ring. Hydrogen atoms on the surface of the catalyst then migrate to the benzene ring and form hydrogenated products, and the Pd catalyst is regenerated. The elimination reaction of the intermediate will split the ether bond to form monomer products and at the same time re-aromatize the benzene ring.

Qi *et al.* (2017) used density functional theory to study the mechanism and kinetics of hydrogenated degradation of lignin. They found that the cleavage rate of diphenyl ether compounds depends on the presence of the H \cdot radical. As long as H \cdot radicals are available, diphenyl ether will quickly and completely split. The cleavage rate of β -O-4 ether bond is slightly slower than that of diphenyl ether, and the carbon-carbon bond cleavage is several

orders of magnitude slower than the ether bond. However, the cleavage rate of carbon-carbon bond of diphenyl methane is faster than carbon-carbon bond of β -5 phenylcoumaran type and β - β' pinosresinol type. This can be attributed to the fact that these condensed carbon-carbon bonds are difficult to crack, and these three carbon-carbon bonds account for half of all the chemical bonds in lignin. This conclusion also explains why lignin model compounds can be completely converted, while only a small amount of natural lignin is converted to monomers and oligomers.

Zhou *et al.* (2020b) used isotope labeling method to probe the reaction mechanism of hydrogenation degradation. They explored the effect of different functional groups on α -C on the reaction path by comparing three different β -O-4 model compounds. They found that the reaction rate increased when the dimer contained a carbonyl group on the α -C and that the molecular hydrogen site of action was in the β -C, which facilitated the breaking of the β -O-4 ether bond. In contrast, when the α -C of the dimer does not contain a functional group or the functional group is a hydroxyl group, the reaction rate is significantly reduced, and the molecular hydrogen will preferentially act on the α -C, which is not conducive to the breakage of the β -O-4 ether bond. Li and Song (2020) prepared a β -O-4 polymer with deuterium incorporated at the α , β , and γ positions, which can better model the plant lignin structure for mechanistic study. They suggest that the mechanism of hydrogenation in Pd/C and Ru/C catalytic systems is the synergistic cleavage of C α -O and C β -O bonds in β -O-4 structure. In Pd/C-catalyzed degradation dimer model experiments, dehydroxylation of α -sites was a side reaction. The same synergistic cleavage mechanism can be inferred from this. They also found that the hydrogenation rate of β -O-4 ether bond was significantly increased by introducing Lewis acid into Pd/C. Therefore, a new catalytic system can be designed to promote hydrogenation by adjusting the content of noble metal or adding cheap metal.

SUMMARY AND OUTLOOK

The extraction of aromatic monomers from lignin can bring additional profits to pulp and paper industry and bioethanol manufacturing industry. Hydrogenated degradation of lignin is considered as one of the most promising and efficient approaches. The study of the hydrogenated degradation of lignin has a long history (about 80 years), and during the long and intensive study of the hydrogenated degradation of lignin, researchers have come to understand the main factors influencing the improvement of monomer yields and the negative impact and importance of dimer and oligomer products on the reaction. How to achieve a high value use of lignin and prevent structural changes in lignin during the reaction are the main challenges to be solved for lignin hydrogenation degradation.

This challenge can be met by studying the hydrogenative degradation of dimer model compounds with different lignin structures. It has been found that the hydrogenative degradation of lignin to phenolic monomers requires the interaction of reaction solvents and catalysts for a highly selective degradation to the target product. This paper also has analyzed and summarized the degradation conditions of real lignin, explored the influence of hydrogenolysis factors on lignin, and analyzed the mechanism of lignin hydrogenolysis. In particular, in order to obtain more monomeric phenolic products, this paper analyzed the possible condensation reactions during hydrogenolysis, explored the mechanism of their occurrence, and summarized strategies to reduce the condensation reactions.

A lot of previous work has been done to improve the monomer yield as well as selectivity, including numerous comparative experiments on the influencing factors involved in hydrogenation degradation (catalyst, reaction solvent, reaction pressure, atmosphere, reaction temperature, *etc.*). However, there are still many areas that are not currently covered. The following are some suggestions for future work:

(a) Due to the fact that lignin is mostly derived from the pulp and paper industry or the bioethanol preparation industry at present, the structure of lignin is seriously changed during the preparation process, and the content of ether bond decreases while the content of carbon-carbon bond increases. At present, the main action site of hydrogenation degradation reaction is the ether bond structure of lignin. Therefore, it is important to find a highly selective catalytic method to activate and break ether bonds as well as carbon-carbon bonds in lignin, which is meaningful to improve the yield of hydrogenation degradation monophenol.

(b) At present, the conditions of the hydrogenolysis reaction should not only focus on noble metal catalyst and high-temperature and high-pressure reaction. The development of cheaper and more selective transition metal catalysts is the primary target. In addition, developing solvents to supply hydrogen or lignin itself to supply hydrogen is the development direction of lignin depolymerization in the future, which can reduce the risk and achieve green development. Meanwhile, it is feasible to develop an effective and cost competitive product separation and purification process, which is conducive to the continuous hydrogenation degradation reaction, and is an important step towards industrialization.

(c) Although there have been a large number of reactions related to the hydrogenation and degradation of lignin, there is still no systematic and comprehensive study on the reaction mechanism and kinetic process so far. For example, it is still unclear why lignin adsorbs to the surface of the catalyst. Furthermore, for single-atom catalysis, which is currently at the forefront of catalytic science, it is not currently applied to the hydrogenation degradation reaction of lignin.

(d) On the whole, the correlation between biomass structure and hydrogenolysis reaction products needs to be further studied in order to design a reaction system for the directed production of phenol. Rapid and reliable qualitative and quantitative techniques need to be developed for the sake of expanding the information of product distribution. At the same time, in order to further explore the reaction path of hydrogenolysis reaction, it is necessary to develop measuring instruments that can detect the intermediate products of hydrogenolysis reaction in situ. To determine reliable and unified kinetic parameters, a more perfect kinetic model is needed for the hydrogenolysis of lignin, so as to accurately predict the distribution of hydrogenolysis products. In order to improve the selectivity of the ideal product, it is important to develop a suitable catalytic system. All the properties of the catalyst need to be considered and the mechanism of the reaction of the reactants at the active site should be explored. For all parameters in the process of hydrolysis reaction, collaborative optimization is required. For example, collaborative optimization of hydrogenolysis conditions and catalytic systems to improve the selectivity of ideal products.

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