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Published in:
Catalysis Today

DOI:
10.1016/j.cattod.2022.06.005

Published: 15/01/2023

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
Sang, Y., Chen, H., Khalifeh, M., & Li, Y. (2023). Catalysis and chemistry of lignin depolymerization in alcohol solvents - A review. *Catalysis Today*, *408*, 168-181. https://doi.org/10.1016/j.cattod.2022.06.005

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Catalysis Today 408 (2023) 168–181

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalysis and chemistry of lignin depolymerization in alcohol solvents - A review

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ARTICLE INFO

Keywords:
Lignocellulosic biomass
Catalysis
Lignin depolymerization
Alcohol

ABSTRACT

The second-generation biofuel strategy aims to fully utilize lignocellulose, which is the major component of the plant cell wall and the most abundant form of renewable organic resources. Among three major components of lignocellulose, i.e. cellulose, hemicellulose and lignin, lignin has been the least utilized one up to now. Nevertheless, lignin depolymerization (LD) to produce aromatic chemicals and fuels has been intensely explored in the recent decade. Alcohols have been the mostly employed solvents in LD reaction, and are also involved into the LD reaction. This review provides an overview of the catalysis and chemistry of LD reaction in alcohols, especially in methanol, ethanol and isopropanol. The recent advances are firstly summarized, and then the roles of alcohol in LD reaction are outlined. The alcohol self-conversions are firstly discussed, and then the roles of alcohol are discussed in four subtopics: supplying hydrogen, depolymerizing lignin, hindering repolymerization and affecting monomer structure. Alcohol and alcohol-derived intermediates provide active hydrogen for reductive catalytic LD reaction carried out without hydrogen input, effectively break ether linkages but not C-C linkages in lignin, and also react with active intermediates and monomers, suppressing the repolymerization side reactions. In addition, alcohol also inhibits the hydrogenation of benzene rings and involves in the formation of products, affecting the structure of monomers. With these understandings, the challenges and opportunities of LD are proposed.

1. Introduction

Lignocellulose is the major component of plant cell wall and the most abundant form of biomass. It composes of three biopolymers, i.e. cellulose, hemicellulose and lignin [1]. In the pulp and paper industry, cellulose has been successfully separated and transformed into paper, an indispensable product of human life, for hundreds of years in a commercial large scale. Converting lignocellulose into chemicals and fuels has been widely explored in recent decades. Cellulose and hemicellulose are accessible to bio and chemical hydrolysis to monosaccharides, which can be further transformed into fuel and chemicals. For instance, the fast development of second-generation (2 G) bioethanol production is a combination of chemical and bioprocesses targeting a full utilization of cellulose and hemicellulose to produce fuel components with high efficiency. However, the valorization of lignin has been a challenge both for the conventional pulp and the rising 2 G biofuel industries due to its stable and complex polymeric structure. Lignin is an amorphous tridimensional polymer, and is mainly built up with three primary units: p-coumaryl (H), coniferyl (G) and sinapyl (S) alcohols which are linked by ether bonds (e.g. 4-O-5, β-O-4 and α-O-4) and C-C bonds (e.g. 5–5, β-1, β-5 and β-β) [2,3]. In addition, lignin in herbaceous feedstocks has high contents of p-coumaric acid (pCA) and ferulic acid (FA) units that are linked to other units by ether and ester bonds [1]. Due to its richness with aromatic rings, lignin is suitable for producing high-valued aromatic chemicals.

For a long history, the only available source of lignin in large commercial scale is provided by the pulp and paper industry. Different pulping process produced different types of lignin, such as Kraft,

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https://doi.org/10.1016/j.cattod.2022.06.005
Received 4 December 2021; Received in revised form 17 May 2022; Accepted 2 June 2022
Available online 8 June 2022
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alkaline and soda lignin as well as lignosulfonates [3]. Kraft pulping is the main pulping process, producing over 90 % of all chemical pulps, and hence Kraft lignin has the largest supply among different types of lignin [3]. Lignin produced in the pulping processes undergoes significant structural modifications and thus are deactivated for the depolymerization reaction [1,4]. Generally, sulfur is enriched in Kraft lignin (1.5–3 % sulfur) due to the employment of Na_2S, which poses a challenge of catalyst poisoning [5]. Enzymatic hydrolysis lignin (EHL) produced as a by-product of 2 G bioethanol production is now growing fast to a large volume available commercial scale waste [5]. Compared to the Kraft lignin, EHL is less modified, and hence more accessible for depolymerization reaction [5]. In addition, many other types of lignin have also been produced in lab-scale, such as organosolv lignin, milled wood lignin and ionic liquid lignin, etc [4].

Catalytic LD in a solvent directly produces high-value small-molecule products without or with little formation of char. Many kinds of solvents have been employed in LD to small molecules. Ionic liquids (ILs) showed a high lignin solubility, and were employed both in lignin isolation and LD reaction, but their high cost and the incompatibility of ILs with commodity fuels were also noticed [6–8]. Containing both hydrophilic group (-OH) and hydrophobic group (benzene ring), most of lignin types are poorly soluble in non-polar solvents, such as alkanes, and strong polar solvents, for instance, water [9,10]. Alcohols have been mostly employed for lignin isolation, viz. producing organosolv lignin, and recently as the solvent in LD reaction, due to their relatively high lignin solubility and low cost [9,11]. Especially, low carbon number alcohols can be derived from biorefinery, e.g. ethanol, isopropanol and n-butanol are produced from lignocellulose fermentation in 2 G bioethanol plants [12–14]. More recent breakthroughs may bring a bio-based route for the production of methanol from demethoxylation of the lignin-derived methoxyphenols [15,16], and ethylene glycol from catalytic conversion of cellulose or cellulosic sugars [17]. Moreover, the low carbon number alcohols are compatible with fuels and have been used as additives to gasoline, improving engine combustion performance [18]. Therefore, the utilization of alcohols as solvents for LD reaction is also compatible with the biorefining processes and may improve the sustainability and profitability of the biorefineries.

In the last decade, considerable works about LD in alcohols were published and several milestone results were achieved, but the roles of alcohol have not been fully analyzed and summarized. In this review, the recent advances are firstly summarized, and then the roles of alcohol in LD reaction are discussed. Finally, the current challenges and opportunities of LD are proposed.

2. Recent advances

2.1. Alcohol as the only reactant with lignin

Alcohols not only serve as solvents but also as reactants for LD reaction, and many articles reported LD reaction in alcohol without other reactants. Several articles examined the non-catalytic LD reaction in alcohol [19–25]. In non-catalytic reaction, lignin can be depolymerized with alcohol into lignin oil containing monomers and oligomers in the temperature range 200–400 °C, while char formation has been a major challenge. For catalytic LD reaction in alcohol, some milestone works achieved complete lignin liquefaction and high monomer yields. In 2010, Barta et al. [26] achieved complete conversion of organosolv lignin without the formation of char with $CuMgAlO_x$ as a catalyst in methanol at 300 °C under Ar atmosphere, and obtained cyclohexyl derivatives as main products. They proposed that the active hydrogens for LD and hydrogenation reactions were produced from methanol reforming. Afterwards, Song et al.[27] depolymerized the lignin in birch wood with Ni/C as a catalyst in methanol at 200 °C under Ar atmosphere, and obtained 54 % phenolic monomers with propylguaiacol and propylsyringol as the main products. They remarked the negative effect of extra gaseous H_2 addition and postulated that the formation of active hydrogen from methanol was easier than that from molecular H_2. Ma et al. [28] firstly achieved the complete conversion of Kraft lignin with α-MoC_{1-x}/AC as a catalyst in ethanol at 280 °C for 6 h in N_2, and obtained 1.64 g/g lignin yield of identified monomers [28]. They also remarked that the addition of H_2 resulted in the decrease of overall monomer yield. Huang et al.[29–31] employed $CuMgAlO_x$ as a catalyst for depolymerization of alkali lignin in ethanol. However, in contrast to the products obtained by Barta et al., their monomers obtained at 380 °C were mainly alkylated mono-aromatics. They proposed that ethanol plays the key role for suppressing repolymerization reactions. Yan et al. [32] made a composite catalyst, with supporting α-MoC_{1-x} on $CuMgAlO_z$, based on the works of Barta, Huang and Ma, and illustrated a significant increase of the yield of aromatic monomers and attributed the result to a synergy effect of the α-MoC_{1-x} and $CuMgAlO_z$ catalysts. Afterwards, Ma et al. [33] and Chen et al.[34] from the same group verified that Mo/Al_2O_3 and Mo_2N/Al_2O_3 catalysts both have high activity for the LD reaction of Kraft lignin in ethanol and obtained similar products as α-MoC_{1-x}/AC.

Several results of catalytic LD in alcohol without another reactant are summarized in Table 1. Ni and noble metal catalysts are commonly used. Pt/C [35], Rh/C [36], Ru/C [37], Ni/C [27,38], and Raney Ni [39] were employed in early works, while recent works focused more on the bimetallic alloy catalysts, such as FeNiB alloy [40], $Ni_{0.5}Co_{0.5}$/C [41], 5Ni-5Re/Nb_2O_5 [42], PtRe/TiO_2 [43], Ni_{50}-Pd_{50}/SBA-15 [44], Ni-Cu/H-Beta [45], and NiCu/C [46]. The higher activities of bimetallic alloy catalysts than that of signal metal catalyst is usually explained by the enhancement of ether linkage adsorption or active hydrogen production. Metal catalysts have also been combined with acid or base catalysts for LD to improve the lignin conversion and monomer yields. For example, H-USY and Raney Ni were used as co-catalysts for the depolymerization of EHL with methanol as a solvent [47]. Ru/C and MgO/ZrO_2 were used as co-catalysts for the depolymerization of Kraft lignin with ethanol as a solvent [48]. Metal oxides as catalysts were also reported. As mentioned above, $CuMgAlO_z$ is an efficient catalyst for LD rection in both methanol and ethanol. The oxides of Mo as well as its diagonal elements (Re and V) and homologous element (W) have been also examined. Zhang et al.[49] reported that ReO_x/AC, WO_x/AC, MoO_x/AC and VO_x/AC catalysts were efficient for the cleavage of β-O-4 linkages in 2-(2-methoxyphenoxy)−1-phenyl ethanol, a lignin model compound in isopropanol at 200 °C under N_2 atmosphere, and ReO_x/AC depolymerized organosolv poplar lignin into 11.4 wt % yields of phenolic monomers under same reaction conditions. Mai et al. [50] employed WO_3/δ-Al_2O_3 for the LD reaction of EHL in ethanol under N_2 atmosphere and obtained aliphatic and aromatic monomers with a total yield of 36.3 wt % at 320 °C for 8 h. They also reported that ethanol was decomposed into H_2 over WO_3/δ-Al_2O_3 during the reaction.

2.2. Together with other reactants

2.2.1. With H_2

The most commonly added reactant is H_2 which produces active hydrogens over catalysts. The roles of active hydrogens are recognized as (1) cleavage of linkages in lignin, i.e., catalytic hydrogenolysis, (2) removing oxygen-containing groups in lignin, i.e., hydrodeoxygenation (HDO) and (3) stabilization of active intermediates to avoid repolymerization [1,3,5]. Therefore, LD reaction with H_2 usually gave a high monomer yield without the formation of char. Nevertheless, the initial H_2 pressure for LD reaction is usually 2–3 MPa, and further increasing the initial H_2 pressure is not favorable for LD reaction, as the excessive H_2 adsorption on catalysts hinders the adsorption of reactants [51–54].

The earliest work of LD with H_2 might date back to the work of Harris et al. [55] in 1938. They depolymerized lignin extracted from aspen wood with copper-chromium mixed oxide as a catalyst in dioxane under H_2 atmosphere in order to elucidate lignin structure. However, the publications about LD in alcohol with H_2 appeared in 2012 [51,56]. Some catalysts used in LD without H_2 were also employed in LD with H_2.

Table 1
LD in alcohol without another reactant[a].

Solvent	Feedstock	Catalyst	Reaction condition	Results	Ref.
Methanol	Organosolv lignin	Cu-doped porous metal oxide	300 °C, 24 h, Ar atmosphere	Monomeric cyclohexyl derivatives	[26]
Methanol	Birch wood	Ni/C	200 °C, 6 h, Ar atmosphere	54 % yield of monophenols	[27]
Methanol/ H_2O (5:2, v-v)	cellulolytic enzyme lignin	H-USY and Raney Ni	270 °C, 0.5 h, N_2 atmosphere	27.9 wt % yield of monophenols	[47]
Methanol/ H_2O (1:2, mol:mol)	Birch wood	Pt/C	230 °C, 3 h, 30 bar N_2	45 % yield of monophenols	[35]
Ethanol	Kraft lignin	α-MoC_{1-x}/AC	280 °C, 6 h, N_2 atmosphere	1.64 g/g yield of monomers, including C6-C10 esters, alcohols, arenes, phenols and benzyl alcohols	[28]
Ethanol	Alkali lignin	$CuMgAlO_x$	380 °C, 8 h, N_2 atmosphere	60 wt % yield of alkylated mono-aromatics	[30]
Ethanol	Kraft lignin	MoC_{1-x}/Cu-$MgAlO_z$	330 °C, 6 h, N_2 atmosphere	575 mg/g yield of aromatic monomers, including benzyl alcohols and arenes	[32]
Ethanol	Kraft lignin	Mo/Al_2O_3	280 °C, 6 h, N_2 atmosphere	1.39 g/g yield of monomers, including alcohols, esters, monophenols, benzyl alcohols and arenes	[33]
Ethanol	Kraft lignin	Mo_2N/Al_2O_3	280 °C, 6 h, N_2 atmosphere	1.19 g/g yield of monomers, including alcohols, esters, monophenols, benzyl alcohols and arenes	[34]
Ethanol	organosolv lignin	B-containing FeNi alloyed	320 °C, 2 h,	Deoxygenation of aliphatic hydroxyl and carbonyls in organosolv lignin	[40]
Ethanol	Kraft lignin	Ru/C and MgO/ ZrO_2	350 °C, 1 h, 3 MPa N_2	5.16 wt % yield of monophenols and 0.94 wt % yield of aliphatic esters	[48]
Ethanol	organosolv lignin	$Ni_{0.5}Co_{0.5}$/C	260 °C, 4 h, 1 MPa N_2	55.2 wt % yield of monophenols	[51]
Ethanol	Kraft lignin	5Ni-5Re/Nb_2O_5	330 °C, 3 h, N_2 atmosphere	27.41 wt % yield of aromatic alcohols and 3.14 wt % yield of monophenols	[42]
Ethanol	silver birch	Ni/C	220 °C, 6 h, Ar atmosphere	~50 wt % yield of monophenols	[38]
Ethanol	EHL	WO_3/δ-Al_2O_3	320 °C, 8 h, N_2 atmosphere	4.76 wt % yield of aliphatic compounds 31.58 wt % yield of aromatic compounds	[50]
Isopropanol/H_2O (7:3, v-v)	poplar wood	Raney Ni	220 °C, 3 h	26 wt % yield of lignin-oil	[39]
Isopropanol	Kraft lignin	Rh/C	350 °C, 4 h	63.8 wt % cyclohexanols and cyclohexanones	[36]
Isopropanol	Lignin obtained from ionic liquid processed biorefinery	Ru/C	300 °C, 3 h, 2 MPa N_2	27 wt % yield of monophenols	[37]
Isopropanol	Organosolv poplar lignin	ReO_x/AC	200 °C, 8 h, under N_2 atmosphere.	11.4 wt % yield of monophenols	[49]
Isopropanol/water (2:1, v-v)	Acid extracted birch lignin	PtRe/TiO_2	240 °C, 12 h, 1.5 MPa He	18.71 wt % yield of monophenols	[43]
Isopropanol/water (2:1, v-v)	Acid extracted birch lignin	$Ni_{50}Pd_{50}$/SBA-15	245 °C, 8 h, 0.5 MPa N_2	18.52 wt % yield of monophenols	[44]
Isopropanol	Kraft lignin	Ni-Cu/H-Beta	330 °C, 3 h, N_2 atmosphere	50.83 wt % yield of cycloalkanes and alkanes	[45]
Ethanol/Isopropanol (1:1, v-v)	Organosolv poplar lignin	NiCu/C	270 °C, 4 h, 1 MPa N_2,	63.4 wt % of monophenols	[46]

[a] These results are classified by solvent and ranked according to their publication time

Song et al.[56] made the effort on LD with Ni/C as a catalyst with H_2 earlier than their work without H_2. They reported 68 wt % lignosulfonate conversion with 20 % selectivity of 4-propyl-guaiacol and 66 % selectivity of 4-ethyl-guaiacol obtained in lignosulfonate depolymerization in ethylene glycol at 200 °C under 5 MPa H_2, and ethylene glycol and glycerol were more efficient as solvents than monohydric alcohols, water and alkanes [56]. Barta et al.[57] also examined the activity of $CuMgAlO_x$ on LD reaction of organosolv lignin with H_2 in methanol after their work about LD without H_2, and obtained 71.2 wt % methanol MeOH-soluble products at 180 °C under 4 MPa H_2. Similar to the reaction without H_2, Ni and noble metal catalysts, such as Ru/C. Pd/C and Pt/C, are often used with H_2 [51,56,58–61]. Recently, Sang et al.[62] prepared an unsupported nickel-based catalyst through nickel formate decomposition, and employed it for LD reaction of EHL in ethanol. After reaction at 280 °C under 2 MPa H_2 for 6 h, 28.5 wt % of phenolic monomers were obtained with complete EHL liquefaction. Mo-based catalysts, including molybdenum oxide, molybdenum sulfide, molybdenum carbide, are also reported [63–68]. For example, Li et al.[63] depolymerized alkali lignin into 72.66 wt % of lignin-oil with MoS_2 as a catalyst in ethanol at 310 °C under 0.5 MPa H_2. Wang et al. [64] found that Ni-Mo_2C/C show higher activity for LD than Mo_2C/C, and obtained 61.3 wt % lignin-oil and 31.94 wt % phenolic monomers with Ni-Mo_2C/C in isopropanol at 250 °C under 2 MPa H_2. Xiao et al.[65] depolymerized enzymatic mild acidolysis lignin into 63 wt % lignin-oil, containing 47 wt % of phenolic monomers, with MoO_3/CNT (carbon nanotube) as a catalyst in methanol at 260 °C under 3 MPa H_2. Their catalyst showed low activity for hydrogenation of carbon-carbon double bands in monomers, giving 62.5 % selectivity of unsaturated monomers [65]. Although methanol, ethanol and isopropanol are most commonly used, the utilization of butanol and the mixture of ethanol or water/-butanol as solvents for LD of organosolv lignin have been also reported [58,61,69], and several articles reported that butanol shows a higher solubility of organosolv lignin than methanol, ethanol and isopropanol [70,71].

The combination of acid/base and metal catalyst has been employed in LD reaction with H_2 to improve lignin conversion and monomer yield. Metal chlorides, as Lewis acids, are often used with metal catalysts in LD reaction [72–75]. For example, Klein et al.[73] investigated the synergistic effect of Pd/C and $ZnCl_2$ catalysts in LD reaction, and assumed that Zn^{2+} coordinated with hydroxyls of β-O-4 linkage, making it easier to be cleaved by hydrogenolysis. Shu et al. [72] found that the addition of $CrCl_3$ significantly improved the degree of lignin liquefaction and overall monomer yield in Pd/C catalyzed depolymerization of alkali lignin in ethanol at 260 ^oC under 4 MPa H_2, and also reported an obvious decrease of monomer yield when Cl^- was replaced with carboanion or NO_3^-. Hence, they thought that Cl^- might serve as a hydrogen bonding acceptor and nucleophilic reagent, weakening the hydrogen-bond and ether linkages in lignin. The addition of soluble base into metal catalyzed LD with H_2 has been also reported. Long et al.[76] reported that the addition of NaOH significantly improved the monomer yield from 6.05 wt % to 12.69 wt % in Ru/C catalyzed depolymerization of organosolv lignin in methanol at 260 ^oC under 4 MPa H_2. Nevertheless, Li et al.[77] reported that the addition of base, such as Cs_2CO_3, CsOAc, KOH and K_2CO_3, results in the decrease of monomer yield but shifts the product distribution form phenols with C3 side chains to those with C2 side chains, in Ru/C catalyzed depolymerization of enzymatic mild acidolysis lignin in methanol at 220 ^oC under 3 MPa H_2.

2.2.2. With Formic acid

Formic acid (FA) decomposes into H_2 or undergoes catalytic transfer hydrogenation over a catalyst [78], and thus several works have described the use of FA as a hydrogen-donor for reductive LD reaction. Meanwhile, FA may also involve into LD reaction as a Brønsted acid catalyst. Therefore, the product yield and distribution obtained in the LD reactions with FA are usually different from those obtained with H_2 or alcohol as the hydrogen-donors. For example, Kristianto et al. [79] reported that the replacement of FA with H_2 resulted in the decrease of the yield of lignin-oil obtained in Ru/C catalyzed depolymerization of acid hydrolysis lignin at 350 °C. Oregui-Bengoechea et al. [80] also found that replacement of FA with H_2 or isopropanol in the NiMo catalyzed depolymerization of EHL at 320 °C resulted in the decrease of oil yield and increase of the solid residue yield. In addition, alkylation of phenolic monomers occurs during the LD reaction with the presence of FA [79–81]. Metal catalysts added also significantly affect the reaction. Oregui-Bengoechea et al. [80] reported that Ru/C catalyst promoted H_2 evolution from FA, and suppressed the esterification reaction between FA and ethanol. Huang et al. [82] found that the Ni/X-zeolite catalyst reduced the molecular weight of products obtained from the depolymerization of Kraft lignin with FA in a H_2O/ethanol mixture at 200 °C, while the catalyst had minor effect on the reaction at 300 °C. Matsagar et al. [83] found Rh/C improved the yield of phenolic monomers and promoted the hydrogenation of alkenyl side chains in monomers in the depolymerization of alkali lignin with Rh/C and FA in H_2O/ethanol (3/1, v/v) mixture at 250 °C [83].

2.2.3. With oxidants

The oxidative LD reactions in alcohol with oxidants, such as O_2, H_2O_2 and ozone, are also explored. In oxidative LD reaction, both the C–O and C–C linkages can be cleaved at temperatures as low as 200 °C, producing aromatic monomers, including aldehydes (p-hydroxybenzaldehyde, vanillin and syringaldehyde), acids (p-hydroxybenzoic, vanillic and syringic acid) and their derived esters [84–92]. Under harsh reaction condition, aromatic rings in products are disrupted, yielding aliphatic carboxylic and dicarboxylic acids as well as CO_2 [84–92]. Vanillin, a widely used flavouring agent, is the most important product of oxidative LD reaction. Nevertheless, the total aromatic monomer yields obtained from oxidative LD reactions are mostly below 20 wt %, and vanillin yields are usually below 10 wt % [84–92].

In 2008, Voitl and Rudolf von Rohr [88] carried out Kraft lignin oxidation with polyoxometalate ($H_3PMo_{12}O_{40}$) as a catalyst and O_2 as oxidant at 170 ^oC in 80 vol % methanol/water solvent, and obtained 2.92 wt % yield of monomers, mainly including vanillin, methyl vanillate, syringaldehyde and methyl syringate. When pure water was used as solvent, the overall monomer yield decreased to 0.2 wt %. Ouyang et al. [90] also reported that the addition of methanol into H_2O also improved the yield of aromatic monomers in the oxidation of alkali lignin with $CuO/Fe_2(SO_4)_3$/NaOH as a composite catalyst and H_2O_2 as the oxidant. The employments of pure methanol and ethanol as solvents were also reported [86,89,91,93]. Deng et al.[89] used methanol as a solvent for oxidation of organosolv lignin with Pd/CeO_2 as a catalyst at 185 °C under 0.1 MPa O_2, producing 5.2 wt% vanillin and 2.4 wt % p-hydroxybenzaldehyde. They thought that oxidation of a C_α-hydroxyl group into a C_α-ketonic group over Pd sites was the first step for cleavage of β-O-4 linkages, and CeO_2 also catalyzed the oxidative cleavage of C_α-C_β bond. Li et al. [86] used ethanol as a solvent for oxidation of organosolv lignin with Ce-Cu/MFI nanosheets as a catalyst at 150 °C under 1 MP O_2, and obtained 5.08 wt % aromatic monomers and 24.32 wt% aliphatic esters. Based on the results of lignin model conversions, they thought that C_α-C_β bonds are preferred to be cleaved instead of C_β-O bonds in their catalytic system. Alcohol solvent also involve into the formation of products. Figueirẽdo et al. [93] examined the oxidation of lignin pyrolysis oil with ozone without catalyst in ^{13}C labeled methanol, and reported that and 19.5 wt % of methoxy groups in products originated from the methanol. They thought that methanol reacted with acids and aldehydes formed in oxidative LD reactions, producing esters and acetals, respectively.

2.3. With lignocellulose as feedstock

The structure of lignin is prone to be changed during lignocellulose fractionation, reducing the reactivity of lignin for depolymerization. To avoid this, a suitable strategy is directly catalytic depolymerization of lignin in native lignocellulose, i.e., catalytic fractionation. As a special LD reaction, catalytic fractionation targets at extraction and depolymerization of lignin simultaneously into lignin-oil rich in monomers, remaining hemicellulose and cellulose in solid residue. Different methods, including reductive catalytic fractionation (RCF), acid-catalyzed fractionation (ACF), and oxidative catalytic fractionation (OCF), have been investigated.

RCF has been intensively investigated, in which, lignin is depolymerized into phenolic monomers and oligomers and extracted into the liquid phase, while most of cellulose and hemicellulose are preserved in solid residue. H_2 is mostly used, although alcohols as the hydrogen-donors are also reported, which has been summarized in Table 1 [27,35,39,94,95]. Sels and his co-workers' works [96–102] gave the basic understanding of RCF reaction. The lignin monomer yield obtained from RCF is mainly depended on the feedstock used [5,103]. Hardwoods, such as birch, poplar and eucalyptus, yield higher phenolic monomers, around 40–55 wt %, than softwood and grass which usually produce 20–25 wt % phenolic monomers, due to the higher content of β-O-4 linkages in hardwood lignin [98]. The feedstock used also determines the structure of the lignin monomers. 4-propanol and 4-propyl substituted methoxyphenols are usually the main products of woody RCF reaction [5,27,52,97–99,101,104–106]. Unique for herbaceous feedstocks is that they have high content of pCA and FA units which are converted to methoxyphenols with ester side-chains during a RCF reaction [107–109]. Sels and his co-workers[96] also found that the delignification degree showed a positive correlation with the polarity of the solvent used, and the high polarity of solvent also enhanced the LD reaction. Therefore, methanol with high polarity and low boiling-temperature is the mostly employed solvent for RCF reaction up to now, irrespective to the feedstock and catalyst [5,52,96–99,101,104, 106–112]. For other alcohols, such as ethanol, isopropanol and n-butanol, as solvents, water is added into the reaction to improve the polarity of solvent and thus enhance the lignin extraction and depolymerization steps [27,100,102], but the addition of water also promotes the solubilization of hemicellulose [100]. Ni, Ru, Pd and Pt metal catalysts are commonly used for RCF reaction, due to their high hydrogenation activity [103], while the employment of Mo-based catalysts, such as MoO_3[111] and MoS_2 [109], and $CuMgAlO_x$[113] was also reported. Nevertheless, different catalysts, such as Ru/C and Pt/C, gave similar phenolic monomer yields under same reaction conditions [97].

In ACF, not only lignin but also most of hemicellulose and part of cellulose are depolymerized, and the main lignin monomers are phenolic monomers containing carbon-carbon double bonds in their side chains [114,115]. Subbotina et al.[114] employed BETA-1 zeolite as a catalyst for ACF of birch wood in a H_2O/ethanol (9:1 v/v) mixed solvent, and obtained 20 wt % phenolic monomers at 220 ^oC for 2 h. Ma et al.

[115] examined the ACF of corn stover with H_2WO_4 as a catalyst in methanol, and obtained 25.1 wt % phenolic monomers at 200 °C for 6 h. ACF and RCF have been combined to improve the delignification degree and lignin monomer yield [99,104,106,107,116]. For example, Parsell et al.[104] reported that the addition of $ZnCl_2$ in Pd/C catalyzed RCF of poplar wood promoted both lignin depolymerization and the removal of hydroxyls in 4-propanol side chains of monomers. Huang et al.[106, 116] explored the role of metal triflates and Pd/C in RCF of birch wood. They thought that metal triflates were more active for the cleavage of chemical bonds between lignin and carbohydrates and β-O-4 linkages in lignin than Pd/C, while Pd/C was responsible for the cleavage of α-O-4, 4-O-5 and β-β linkages [106,116].

Very recently, OCF of lignocellulose were reported. Different from RCF and ACF, the lignin monomers produced in OCF are aromatic acids, ester and aldehyde, instead of phenolics. Du et al.[117] performed a two-step OCF of sawdust wood in a CH_3OH/H_2O (9:1) mixture under 10 bar oxygen/nitrogen (9:1) with polyoxometalate as the only catalyst. In their reaction, 96 % lignin was extracted and stabilized through methoxylation at 100 °C in the first step and then further depolymerized into 45.9 wt % aromatic monomers at 140 °C in the second step. Nearly at the same time, Hao et al.[118] reported a one-step OCF of lignocellulose at 190 °C under 35 bar 6 % O_2 in N_2 in acetone with Co-containing nitrogen-doped carbon catalysts (Co-N-C) as a catalyst. Nevertheless, the aromatic monomer yields they obtained with different lignocellulose (poplar, pine and miscanthus) were in the range of 8–15 wt %, much lower than that obtained from RCF reaction.

3. Alcohol self-conversion

In LD with alcohol as a solvent. alcohol self-conversion reactions also occur, and the intermediates formed from alcohol self-conversion reactions also involve into LD reaction. Therefore, several articles reported that the yield of products obtained from LD reactions exceeded 100 wt %. For instance, Ma et al.[28] obtained 1.64 g/g lignin of products, including both aromatic products (arenes, benzyl alcohols and phenols) and aliphatic products (alcohols and esters), from α-MoC_2 catalyzed Kraft lignin depolymerization in supercritical ethanol at 280 °C. After that, Yan et al.[32] detected the aliphatic oxygenates and alkenes (Fig. 1 (a)) in α-$MoC_{1-x}/CuMgAlO_x$ catalyzed ethanol self-conversion reactions without lignin input at 330 °C. When Kraft lignin was added, these aliphatic products become more complex and lignin derived aromatics contained alkyl and alkoxy groups which may be derived from ethanol (Fig. 1(b)). They also noticed that the yields of lignin derived aromatic monomers increased with the increase of the yields of ethanol derived aliphatic oxygenates, and hence proposed that LD reaction was promoted with the intermediates formed from ethanol self-conversions [32]. Self-conversion reactions of supercritical alcohols also occur without adding a catalyst. Riaz et al.[81] reported that the self-conversion of methanol, ethanol, and isopropanol at 350 °C without a catalyst were 3.6, 11.1, and 7.4 wt %, respectively, while alcohol self-conversions were significantly promoted when a Ru/Al_2O_3 catalyst was added into the reaction.

The reaction mechanisms of alcohol self-conversions during LD reactions have been discussed in several articles [23,81,119,120]. Dehydrogenation of alcohol into aldehyde or ketone is supposed to be the first step for the formation of higher alcohols, esters and acetals (Fig. 2(a)). Aldol condensation reaction occurs between two aldehydes or ketones, and the product formed further undergoes dehydration and hydrogenation reactions, with formation of higher alcohols. For example, the process of butanol formation is shown in Fig. 2(b). Esters are formed through Tishchenko reactions of two aldehydes or ketones, as shown in the process of ethyl acetate formation (Fig. 2(c)). Both Tishchenko reaction and aldol condensation are catalyzed by basic sites of catalyst or bases existing in lignin. Alkali lignin and Kraft lignin contain high amounts of bases as impurities. Acetals are formed from acid-catalyzed reactions. Aldehyde or ketone is activated by H^+, and then undergoes a condensation reaction with an alcohol, with formation of hemiacetal. Hemiacetal is transformed into acetal through etherification reaction

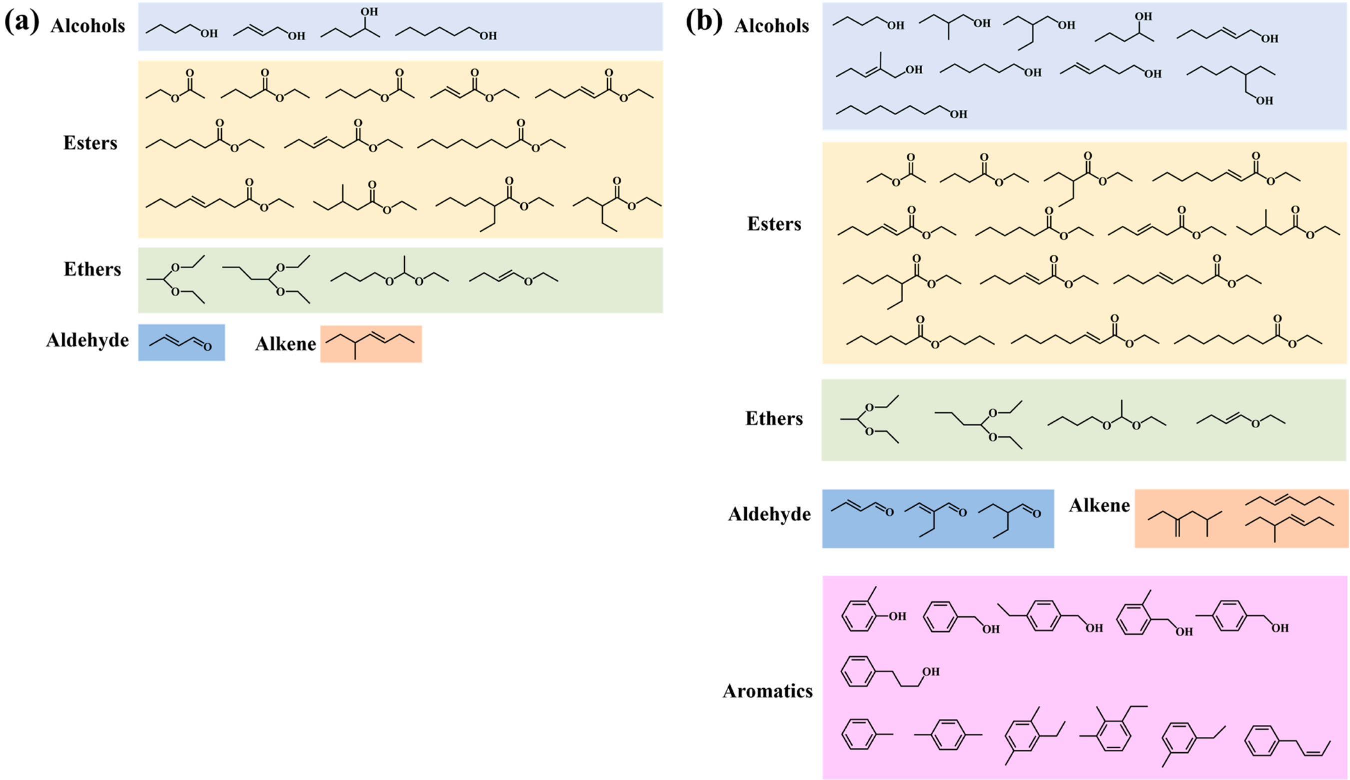

Fig. 1. (a) Products obtained from α-$MoC_{1-x}/CuMgAlO_x$ catalyzed ethanol self-conversions at 330 °C for 6 h. (b) Products obtained from α-$MoC_{1-x}/CuMgAlO_x$ catalyzed depolymerization of Kraft lignin in ethanol at 330 °C for 6 h.

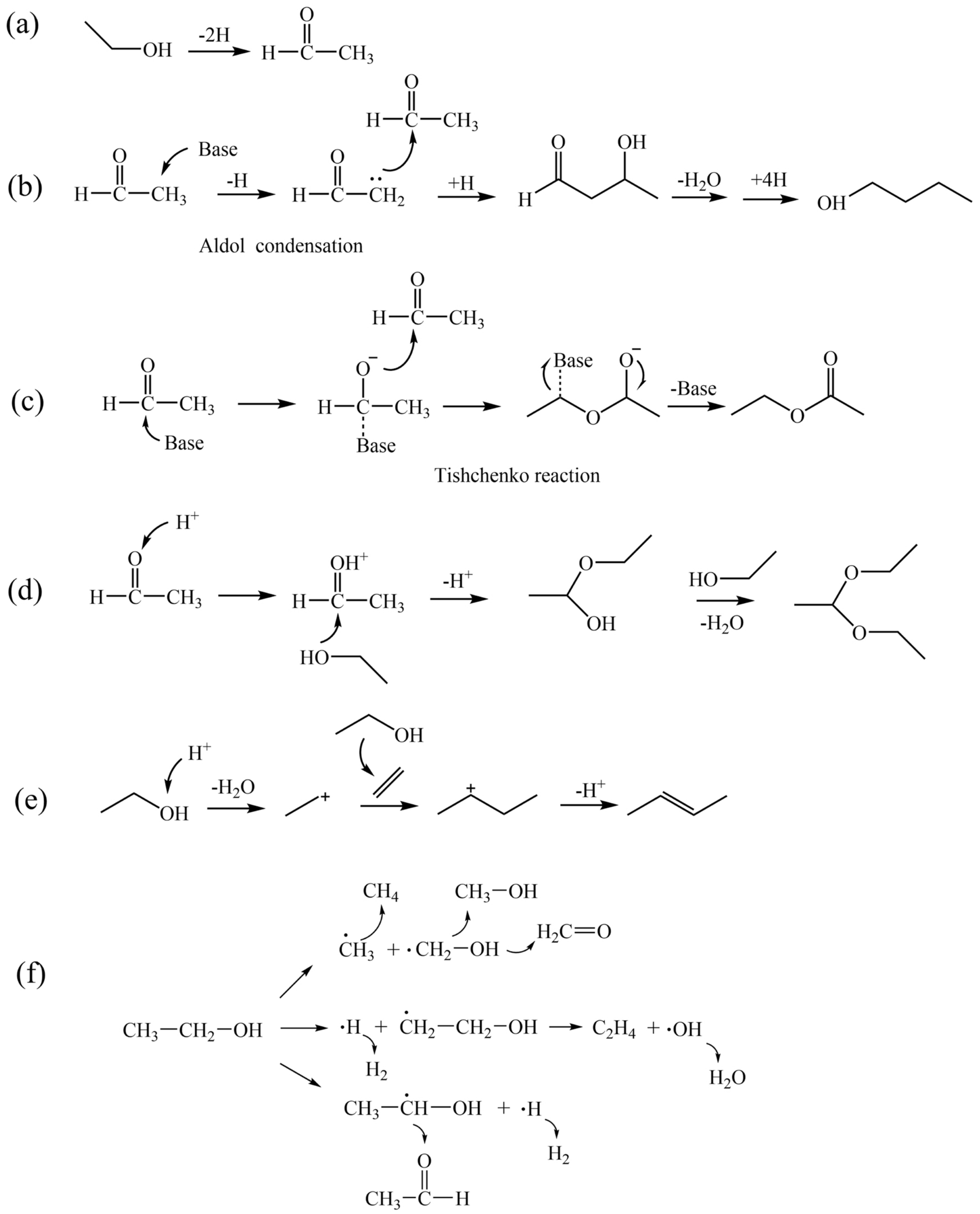

Fig. 2. The reaction mechanisms of ethanol self-conversions to acetaldehyde (a), butanol (b), ethyl acetate (c), ethyl acetal (d) and propene (e) and reaction mechanisms of free radical initiated ethanol self-conversions (f).

with an alcohol. For example, the formation of ethyl acetal is shown in Fig. 2(d). In addition, carbonium ions formed in acid catalyzed reaction also undergo C-C coupling reaction with alkenes formed from dehydration of alcohols, producing higher aliphatic hydrocarbons. For example, the formation of propene is shown in Fig. 2(e). Bansal and Freeman[121] verified that the non-catalytic self-conversion of ethanol at above 280 °C follow a radical mechanism through addition of a free-radical scavenger into the reaction system. The processes for the formation of hydrogen, acetaldehyde, methane, formaldehyde, methanol, and ethylene in non-catalytic ethanol self-conversion reactions are shown in Fig. 2(f).

The common reaction conditions for LD reaction (250–350 °C, 10–20 MPa) usually exceed the critical points of the common alcohol solvents (methanol: 240.0 °C, 8.1 MPa; ethanol: 241.0 °C, 6.3 MPa; isopropanol: 236.0 °C, 4.9 MPa). Under supercritical conditions, alcohols have several advantages for LD reaction, such as high lignin solubility, high heat transfer and high dispersion capacity, and the alcohol self-conversions are also significantly promoted [10,81]. The radicals, carbonium ions, aldehydes and ketones formed from alcohol self-conversions involve into the LD reaction, promoting the cleavage of linkages in lignin and stabilizing active intermediates, as discussed in the following sections. With the increase of the carbon number, the critical temperature generally increases. For example, the critical temperature of n-butanol is up to 289.0 °C. Due to the advantages of supercritical alcohols for LD reaction, low carbon chain alcohols, e.g., methanol, ethanol and isopropanol, are more commonly used than long carbon chain alcohols.

4. Role of alcohol in lignin depolymerization reaction

4.1. Supplying hydrogen

An important role of alcohol in the LD reaction has been recognized as providing hydrogen for the reductive catalytic LD steps. This greatly benefits a real process with avoiding the safety issues of transportation, storage and use of gaseous H_2.

4.1.1. Without another reactant

One reaction mechanism for alcohol to provide active hydrogen is catalytic transfer hydrogenation. Both acid-base sites and metal sites of catalyst show the activity for catalytic transfer hydrogenation [78]. Nevertheless, acid-base sites are only efficient for hydrogenation of carbonyl group into hydroxyl, and metal sites have the ability for cleaving ether bonds [78]. In metal catalyzed reaction, alcohol adsorbs and dissociates into active atomic hydrogen and alkoxyl group over metal sites, and the active atomic hydrogen transforms to a substrate molecule [78]. Isopropanol, as a secondary alcohol, shows a higher activity in dehydrogenation over a metal surface than the primary alcohols, due to the enhanced stabilization effect on the carbocation from two alkyl groups [78]. Rinaldi and his co-workers[122–124] investigated the hydrogenation of lignin monomers and postulated that the alkoxyl group formed from the dissociation of primary alcohol strongly adsorbed on the Raney Ni, blocking the active Ni sites, while the O-H and the C-H in isopropanol were both cleaved on the Raney Ni, forming two active hydrogens and leaving Raney Ni surface unblocked by releasing acetone. They further verified the competitive adsorption of various alcohols and phenol at the interface of Raney Ni with the aid of an ATR-IR technique [124]. The formation of acetone was also reported in LD reactions with isopropanol as a solvent [45,46,49]. Therefore, catalytic transfer hydrogenation might be the main reaction mechanism for isopropanol to provide active hydrogen for LD reaction. Hydrogenolysis of ether linkages and hydrogenation of benzene rings in lignin model compounds through catalytic transfer hydrogenation with isopropanol as a hydrogen donor readily occur at 120 °C [123,125], but the reaction temperature for LD reactions with isopropanol as a hydrogen donor usually exceeds the supercritical temperature of isopropanol, which is 236.0 °C, as summarized in Table 1. This may be because that supercritical isopropanol is essential for efficient lignin dissolution [122].

Barta et al. [26] proposed that the hydrogen for lignin hydrogenolysis and hydrogenation was originated from methanol reforming over $CuMgAlO_x$. Colleagues afterwards also thought that methanol reforming or ethanol reforming supplied hydrogen for the LD reaction in H_2O/methanol or H_2O/ethanol mixtures [35,47,94,126,127]. Alcohol reforming also involves alcohol adsorption and dissociation over a metal catalyst, but, different from catalytic transfer hydrogenation, the O–H, C–H, and C–C bonds in alcohol are cleaved in alcohol reforming. The fragments formed from alcohol are transformed into H_2 and CO_2 with H_2O (water-gas shift), or recombined into H_2, CH_4 and CO without H_2O [128]. As not only O-H bond but also C–H and C–C bonds in alcohol are cleaved during alcohol reforming, the reaction temperature of alcohol reforming is usually higher than that of catalytic transfer hydrogenation. Ouyang et al.[35] investigated the methanol reforming steps in $Pt/\gamma\text{-}Al_2O_3$ catalyzed LD reaction in H_2O/methanol mixture, and found that methanol reforming was actually efficient when the reaction temperature was above 230 °C. Liu et al.[94] also verified that the supplying of hydrogen for LD reaction via methanol reforming on a Pt/C catalyst was not favorable at 190 °C.

Li and his co-workers [28,32,119] thought that the active hydrogens for LD reaction in ethanol may be hydrogen free radicals produced from the supercritical ethanol decomposition at 280 °C. The formation of ethanol derived hydrogen free radicals is also supported with the experiments of Bansal and Freeman [121], as mentioned above. Recently, several articles reported that non-catalytic hydrogenolysis and hydrogenation reactions occurred in methanol at low reaction temperature [77,115]. Li et al.[77] found that methanol provided hydrogen for β-O-4 linkage hydrogenolysis in a non-catalytic reaction at 160 °C, with methanol transforming into formaldehyde. Ma et al. [115] reported that the C═C bond in 4-vinyl phenol and 4-vinyl guaiacol was fully saturated in methanol at 200 °C without a catalyst. However, the reaction mechanisms for these reactions are still unclear.

4.1.2. With H_2, formic acid and O_2

Although Song et al. [27] and Ma et al. [28] remarked that H_2 had negligible impact on monomer production, several articles reported that H_2 was favorable for LD reaction, especially when Ni metal catalysts and noble metal catalysts were used [51–54]. This may be because that Ni and noble metal catalysts have high activities for H_2 activation. Actually, operando NMR analysis revealed that the initially adsorbed H over Ni/Al_2O_3 at 150–175 °C was supply by H_2, instead of isopropanol, while hydroxyl group of isopropanol underwent rapid H exchange with the adsorbed H [129]. Nevertheless, Cao et al.[130] thought that different hydrogen species were formed from isopropanol and H_2, as they found that benzene rings in products were much more easily hydrogenated with H_2 as a hydrogen donor than that with isopropanol as a hydrogen donor, in Ru/C catalyzed benzyl phenyl ether conversion in isopropanol at 200 °C with or without 1 MPa H_2.

Riaz et al. [81] tried to verify whether the hydrogen for catalytic depolymerization of alkali lignin came from alcohol or FA. They found that the amounts of H_2 produced from methanol, ethanol and isopropanol at 350 °C were 0.71, 4.75, and 20.70 mmol/60 g alcohol, respectively, while the amount of H_2 produced from the decomposition of FA was 127.1 mmol H_2/60 g FA, much higher than those from the alcohols [81]. They further examined the reaction with the molecular simulation and postulated that the hydrogen for LD mainly comes from FA decomposition instead of from the alcohols [81].

Under O_2 atmosphere, alcohol may also provide active hydrogen for LD reaction, proposed by Tana et al. [131] In their reaction, lignin in raw sugarcane bagasse was depolymerized with Pd/C as a catalyst under O_2 atmosphere in methanol or ethanol at 250 °C. Instead of aromatic acids, ester and aldehyde which usually formed from oxidation reaction, the main lignin monomers obtained were typical products formed from reductive reaction, which mainly included para-alkylated phenols and esters derived from ferulic and p-coumaric acids, and the monomer yield obtained under O_2 atmosphere was much higher than that obtained under Ar atmosphere. Hence, they proposed that the LD reaction was underwent through hydrogenolysis with active hydrogens produced from the oxidation of alcohol to aldehyde over the surface of Pd/C catalyst.

4.2. Involving in depolymerization steps

4.2.1. Fragmentation-depolymerization process

For catalytic reductive LD reaction in methanol, Song et al. [27] proposed a fragmentation-depolymerization process. They found that lignin fragments in the range of *m/z* 1100–1600 were formed in non-catalytic reaction in methanol at 200 °C, and these fragments disappeared with formation of monomers when adding the Ni/C catalyst. Therefore, they postulated that lignin was firstly fragmented into smaller segments through non-catalytic methanolysis, and then these segments further depolymerized into monomers and oligomers on the catalyst. Ma et al. [119] investigated the reaction pathways of Kraft lignin depolymerization over Mo-based catalysts, including MoO_3/Al_2O_3, Mo_2N/Al_2O_3, Mo/Al_2O_3 and $\alpha\text{-}Mo_{1-x}C/AC$, in ethanol at 280 °C under N_2 atmosphere, and also gave evidence that Kraft lignin was firstly depolymerized into fragments, and then the fragments were converted into monomers with a catalyst. Moreover, they proposed that ethanol promoted the dissociation of Mo species from the solid Mo-based catalysts into the fluid phase, forming molybdenum ethoxides which behaved as the active species for the further fracturing of lignin fragments into final products.

4.2.2. Cleavage of ether linkages

Recently, HSQC NMR is employed for examining the cleavage of linkages in lignin before and after LD reaction. Van den Bosch et al. [101] found that the cleavage of β-O-4 linkages in birch wood lignin was mainly achieved through non-catalytic reaction in methanol at 250 °C, and the addition of Ni/Al_2O_3 catalyst had a little effect on this reaction. Sang et al. [132] also reported the all of the ether linkages in EHL were completely cleavage in non-catalytic reaction in ethanol at 280 °C. However, Anderson et al.[133] reported that, when the reaction temperature was lower than 200 °C, the non-catalytic cleavage of β-O-4 linkages in poplar wood lignin was not efficient.

Non-catalytic cleavage of ether linkages may undergo through two reaction mechanisms. One is that homolysis of ether linkages in lignin occurs at heated condition. The conversion of lignin model compounds containing β-O-4 linkages revealed that compounds with phenolic hydroxyl end-units readily underwent homolysis at around 200 °C, but homolysis of compounds with methoxy end-units were difficult, as the homolysis reaction followed a quinone methide intermediate [134,135]. Another reaction mechanism is that alcohol solvent involves into LD reaction and promote the cleavage of ether linkages in lignin. Li and his co-workers [28,32,119] thought that radicals produced from the supercritical ethanol decomposition may attack and cleave the linkages of lignin. Recently, the evidence of methanol involving into the cleavage of β-O-4 linkages at 160 °C was provided by Li et al.[77] They thought that the non-catalytic cleavage of β-O-4 linkage in 1-(4-(benzyloxy)–3-methoxyphenyl)ethenone in methanol at 160 °C did not follow a radical mechanism, as the addition of radical scavengers did not affect the reaction. The deuterated experiment further verified that the reaction underwent through a non-catalytic hydrogenolysis with methanol providing hydrogen. However, LD reaction may not follow the same reaction mechanism proposed by Li et al., as LD reaction usually curried out at high reaction temperature.

4.2.3. Cleavage of C-C linkages

Compared to ether linkages, C-C linkages in lignin, such as β-β, β-1, β-5 and 5–5, are more stable and more difficult to be cleaved, due to their higher bond dissociation energies [136]. Minami et al. [137] examined the non-catalytic methanolysis of several lignin model compounds, and found that both the α-O-4 and β-O-4 linkages in lignin model compounds were rapidly cleaved at 270 ^{o}C, while the C-C linkages, such as β-1 and 5–5 remained stable. Cheng et al. [24] examined the non-catalytic LD reaction of organosolv lignin in the mixture of ethanol and isopropanol at 270 °C, and found that α-O-4 and β-O-4 linkages were rapidly cleaved but β-β and β-5 linkages remained intact after the reaction. However, several recent articles claimed that C-C linkages in lignin were cleaved after catalytic reductive LD reactions, based on the HSQC NMR analysis [46,49,132]. For example, Sang et al. [132] reported that the NMR signals ascribed to β-5 linked structure disappeared after catalytic reductive LD reaction in ethanol with Ni as a catalyst, but these NMR signals were observed in non-catalytic reaction. The conversion of lignin model compounds and density functional theory simulation has also been performed to examine the cleavage of C-C linkages. Shuai et al.[138] reported that the C-C linkage in dimethylguaiacylmethane, a lignin dimer, was cleaved with CoS_2 as a catalyst at 250 °C under 5 MPa H_2 with formation of phenolic monomers, and found that the catalyst as well as H_2 and phenolic hydroxyl were necessary for the cleavage of C-C linkage. Cheng et al. [139] investigated the adsorption of C-C linkages in lignin model compounds over a catalyst through density functional theory simulation, and found that the bond dissociation energy of C-C linkages was reduced on the Ni (100) and Cu (100) surface involving the coverage of hydrogen. These results suggest that catalysts play a role for the cleavage of C-C linkages, while the reaction mechanism is still unclear.

4.3. Hindering repolymerization

4.3.1. In acid and base catalyzed reaction

The reaction pathways for acid and base catalyzed cleavage of β-O-4 ether bonds have been discussed in previous review articles, and are shown in Fig. 3 [1,3]. For H^+ catalyzed reaction, the first step is the formation of a benzylic carbanion by removal of the OH-group on the α-position. Then, the benzylic carbanion is transformed into enol-ether structure A with removal of a formaldehyde or enol-ether structure B without removal of a formaldehyde. The cleavages of ether linkages in the two enol-ether structures yield C2-aldehyde substituted phenolics and C3-ketone substituted phenolics, respectively. For base catalyzed reaction, quinone methide is supposed to be an intermediate that undergoes ether bond cleavage with formation of monomers. Quinone methide can be also transformed into the enol-ether structure A with removal of a formaldehyde, but, in a base catalyzed reaction, the cleavage of ether linkages in enol-ether structure A does not readily occur [77].

The reaction pathways for repolymerization reaction and stabilization of active monomers and intermediates with alcohols are also shown in Fig. 3. In acid catalyzed reaction, the ortho- and para- positions of benzene ring and phenolic hydroxyl in monomers have higher electron density than other positions, and hence readily react with benzylic carbanion, leading to repolymerization reaction [140,141]. Primary alcohol, e.g. ethanol, acts as a nucleophilic specie and stabilizes benzylic carbanion through alkoxylation, hence suppressing repolymerization reaction [142–145]. The C2-aldehyde substituted phenolics have high activity for repolymerization reaction, but can be stabilized with methanol and ethylene glycol with formation of acetals, following a similar reaction mechanism shown in Fig. 2(d) [146–148]. In base catalyzed reaction, quinone methide readily undergoes addition reaction with an electron-rich benzene ring or phenolic hydroxyl in monomers, and formaldehyde also readily reacts with benzene ring to form a hydroxymethyl group which further form a methylene bridge with another benzene ring [1]. Huang et al. [29,31] put forward that the formaldehyde-induced repolymerization can be suppressed with ethanol. Similar to the formation of butanol (Fig. 1(b)), acetaldehyde generated from ethanol dehydrogenation undergoes aldol condensation with formaldehyde, and the aldehyde formed in aldol condensation further undergoes dehydration and hydrogenation reactions, transforming into a higher alcohol [149].

Huang et al. [29,31] also put forward that etherification and alkylation reactions of phenolic monomers with ethanol in LD reaction efficiently suppressed repolymerization reaction. They verified this statement with the repolymerization reaction of phenol, o-cresol, 2,4,6-trimethylphenol and anisole, and found that one methyl group at the ortho-position significantly suppressed the repolymerization reaction, and three methyl groups at ortho- and para-positions as well as etherification of phenolic hydroxyl group completely suppressed the repolymerization reaction [31]. Interestingly, not only methylated and ethylated products but also isopropylated and even tert-butylated products are usually formed in methanol and ethanol solvent [50,120,150,151]. Recently, Li and his co-works [152–156] investigated the conversion of guaiacol into alkylphenols, such as ethyl, isopropyl and tert-butyl phenols. Two reaction pathways for the formation of higher alkylphenols were proposed. In MoO_3, Re_2O_7, H_2WO_4 and MoS_2 catalyzed reaction with ethanol as a solvent, they proposed that higher alkylphenols were formed from the addition of methyl or ethyl to the alkyl side chains of lower alkylphenols (Fig. 4(a)) [152,154–156]. They thought that the H on the α-carbon was activated by the furious inducement effect of benzene ring and was easily removed with the catalyst. Then, methyl or ethyl formed from ethanol decomposition was

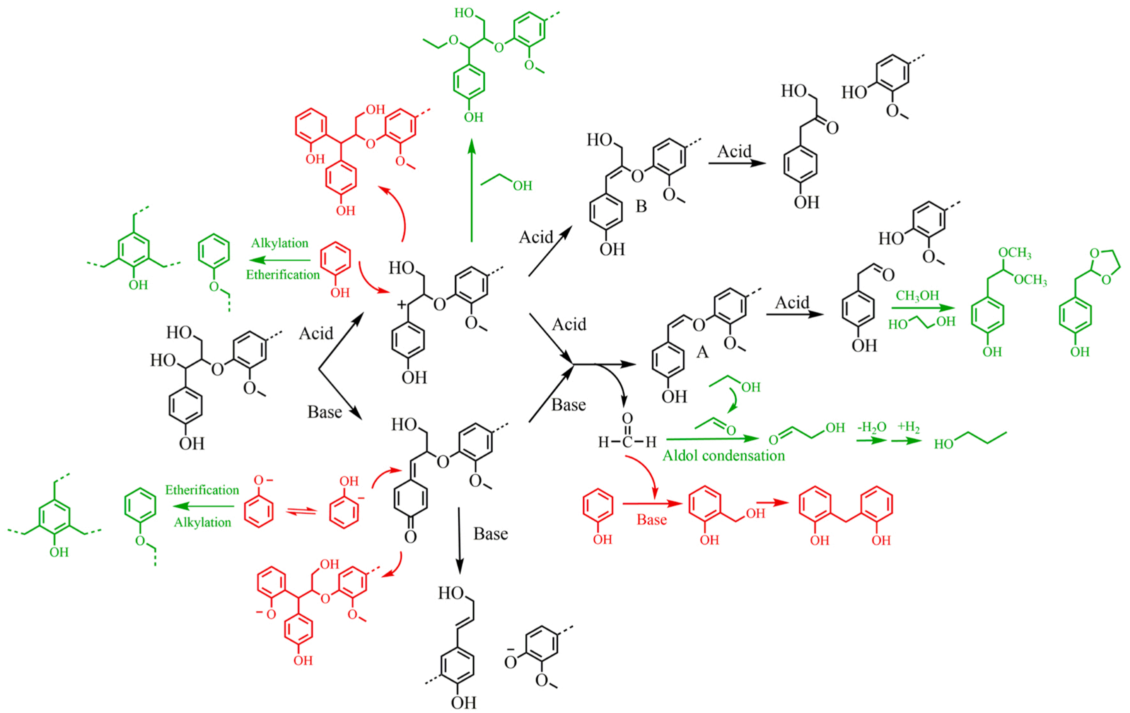

Fig. 3. Reaction pathways for acid and base catalyzed cleavage of β-O-4 ether bonds (black) and repolymerization reactions (red) as well as stabilization of active monomers and intermediates by alcohols (green).

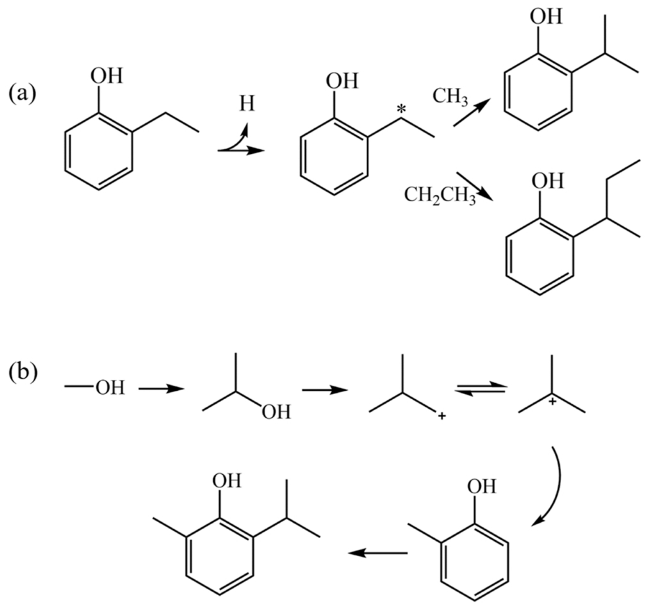

Fig. 4. Reaction pathways of lower alkylphenols to higher alkylphenols. (a) In MoO_3, Re_2O_7, H_2WO_4 and MoS_2 catalyzed reaction with ethanol as a solvent. (b) In V_2O_5 catalyzed reaction with methanol as a solvent,.

attached to α-carbon. In V_2O_5 catalyzed reaction with methanol as a solvent, They proposed that higher alkylphenols were formed from the alkylation reaction between higher alcohol and phenols [153]. They thought that propanol and iso-butanol were firstly produced from methanol conversion, and then transformed into carbocation over Lewis acid sites of catalyst, and finally reacted with aromatic rings in phenols.

4.3.2. Free radical induced reaction

Oxidative LD reaction follows a radical mechanism, and radicals formed during the reaction also initiates repolymerization [3]. As mentioned above, several researchers reported that the addition of methanol suppressed repolymerization reaction and improved monomers yields [88,90,92]. Voitl and Rudolf von Rohr [88] proposed that methanol served as a radical scavenger in oxidative LD reaction, suppressing the repolymerization. Nevertheless, they thought that the formation of $CH_3O^\bullet$ and $H^\bullet$ through homolytic cleavage of the OH bond in methanol was not readily due to the high bond dissociation energy (105 kcal/mol), and proposed that methanol first formed dimethyl ether on strong Brønsted acid site of $H_3PMo_{12}O_{40}$, and homolytic cleavage of C-O bond in dimethyl ether occurred with formation of $CH_3O^\bullet$ and $CH_3^\bullet$ radicals as a result of the relatively low bond dissociation energy (84 kcal/mol).

Except oxidative LD reaction, other type LD reactions, i.e., reductive LD reaction and acid and base catalyzed reaction are usually carried out at around 300 °C. At such high temperature, the products formed from LD reaction, e.g., guaiacol, are decomposed into free radicals, which readily undergo repolymerization reaction [157]. H_2 is supposed to be a radical scavenger, and inhibits free radical induced repolymerization. Alcohols can serve as hydrogen donor, producing H_2 or active H, during LD reaction, and hence alcohols are also supposed to play a role for suppressing free radical induced repolymerization. For example, Kim et al. [20] found that higher yields of monomers and lower yields of char were obtained in isopropanol than that in naphthalene, in non-catalytic LD at 400 °C, and thought that the active hydrogens produced from isopropanol suppressed the repolymerization reaction. As not only hydrogen free radicals but also alkyl radicals, such as methyl and ethyl, are formed from supercritical ethanol decomposition [121], Li and his co-workers [28,32,119] proposed that both hydrogen and alkyl radicals from supercritical ethanol decomposition reacted with free radicals formed from LD reaction, suppressing repolymerization reaction.

4.4. Affecting monomer structure

With alcohol as a solvent, phenolic monomers are usually formed in reductive LD reaction [3], although several articles also reported the hydrogenation of benzene rings at relative high temperature [26,36]. Nevertheless, cycloalkanes are the main products when alkane is used as a solvent [158–162]. For example, Li and his co-workers[163,164] reported that EHL was depolymerized into phenolic monomers in ethanol with $NiMo/Al_2O_3$ as a catalyst at 320 °C under 2.7 MPa H_2, but only cycloalkanes were detected in cyclohexane with the same catalyst under the same reaction conditions. The inhibition of benzene ring hydrogenation was also reported in other oxygenated solvents, e.g., 1,4-dioxane [165]. Nevertheless, no detailed mechanism has been discussed up to now. We speculate that the competitive adsorption of the oxygenated solvent on the catalyst may inhibit the adsorption of benzene rings in phenolic monomers.

Due to involving into LD reaction, alcohol solvent also affects the structure of monomers, especially for the LD reaction without other reactants. Ma et al.[28] found that arenes, benzyl alcohols and phenols were formed in α-MoC_2 catalyzed Kraft lignin depolymerization with ethanol as a solvent, while almost only phenols were detected when methanol and isopropanol were used. In addition, Cui et al. [152] reported that ethanol was more efficient than methanol and isopropanol for MoO_3 catalyzed guaiacol alkylation. In ethanol, ethyl, isopropyl and tert-butyl phenols were formed as main products, while mainly methyl phenols and isopropyl phenols were produced in methanol and isopropanol, respectively. These results indicate that ethanol is more active for involving into the LD reaction, which may be due to its capacity to create methyl and ethyl groups simultaneously in reaction. For LD reaction with H_2, the effect of alcohol solvent on the monomer structure is less pronounced. Sang et al. [62] examined the relationship between the structure of monomers and the alcohol solvent used in Ni catalyzed reductive LD reaction of EHL. They found that the structures of ester monomers were dependent on the solvent used, while the para-alkyl side chains of phenolic monomers, i.e., para-methyl, para-ethyl, para-propyl, were independent on the solvent used (Fig. 5(a)). They proposed that ester monomers were formed through the esterification reaction of acids (FA and pCA) released from EHL and alcohol solvent, and the para-alkyl side chains of phenolic monomers were original from the side chains of primary monomers (G and S) in EHL, instead of alkylation reaction of solvent (Fig. 5(b)). In oxidative LD reaction, the structure of esters obtained are also dependent on the alcohol solvent used, as these esters are also formed from the esterification of acids produced from oxidative LD reaction and alcohol solvent [88,166].

5. Conclusion and perspectives

Pulp and paper industry and 2 G biorefinery produce lignin in large commercial scale. The depolymerization of lignin produced from paper industry has been intensively investigated in the last decade. However, with the development of 2 G biorefinery, EHL depolymerization will become a focus in the near future to improve the sustainability and profitability of the 2 G biorefinery. For the sake of improving profitability and sustainability of the 2 G biorefinery, ethanol, as the main product of 2 G biorefinery is favored as the solvent for LD reaction. Ethanol is environmentally benign and compatible with gasoline fuel. Nevertheless, biomass catalytic solvolysis has both wide availability and diversity of feeds and possibility of producing many commodity fuel products. While developing the techniques with using ethanol as the solvent, the other fuel compatible and environmentally benign solvents should be explored.

Alcohols has been up to now the most successful solvents for catalytic LD reaction, achieving complete conversion without formation of tar and char residues. Alcohol conversions occur during LD reaction, and the intermediates and products formed from alcohol conversions also involve into the LD reaction. Reductive catalytic LD reaction can be achieved with alcohol as hydrogen-donor via catalytic hydrogen transfer and alcohol reforming steps, avoiding the safety issues of using gaseous H_2. The fragmentation-depolymerization process for catalytic LD reaction has been generally accepted. In this process, alcohol depolymerizes lignin to fragments and monomers, which are further converted over a catalyst. Recent results reveal that alcohol mainly promotes the cleavage of ether linkages in lignin. Alcohol also stabilizes active intermediates and monomers, and serves as radical scavenger, suppressing the repolymerization.

Up to now, most of the reaction mechanisms proposed for LD reaction have not been verified yet. In-situ/operando characterization analysis, such as NMR, has been employed for revealing the reaction steps of lignin model compound reaction. However, these techniques have not yet been used for LD in alcohol. In addition, only molecular weight of lignin fragments formed in LD reaction are analyzed, but exact structures of lignin fragments are still not clear. Therefore, in-situ/operando characterization analysis and characterization of structures of lignin fragments is highly demanded for solidifying the reaction mechanism of LD in alcohols. Catalyst plays a minor role for the cleavage

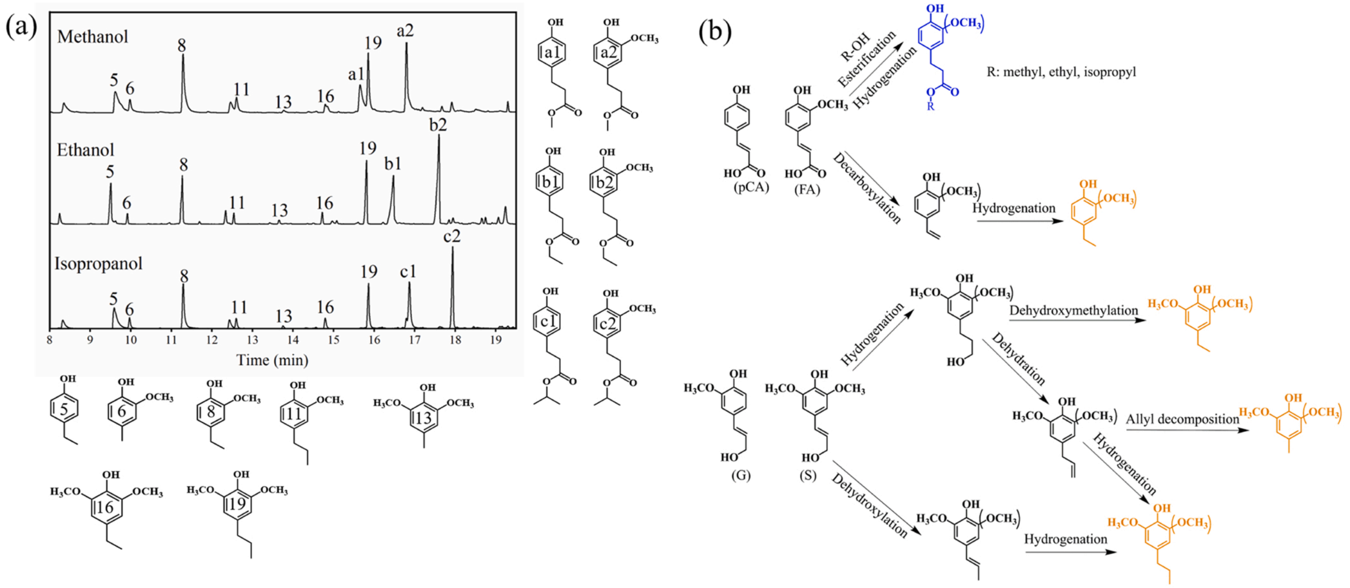

Fig. 5. (a) the relationship between the structure of monomers and the alcohol solvent in Ni catalyzed reductive LD reaction of EHL. (b) The processes for formation of esters and para-alkyl phenols.

of ether linkages at and above 250 ^{o}C in lignin alcoholysis but may promotes the cleavage of C-C linkages. Hence, future investigation should be fucus on how to improve the activity of catalyst for the cleavage of C-C linkages. Although repolymerization reaction is partly suppressed through the reaction of alcohol with active intermediates, it is still one of the main limitations for lignin liquefaction and high monomer yield. Hence the mechanism of repolymerization reaction and new strategy for suppressing repolymerization need to be further investigated.

CRediT authorship contribution statement

Mohamad Khalifeh made a literature survey and wrote a draft manuscript on the topic under the supervision of Hong Chen. Yushuai Sang made intensive input with verifying each key point and rewrote the manuscript. Yongdan Li and Hong Chen finalized the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work has received funding from the European Union's Horizon 2020 research and innovation program, (BUILDING A LOW-CARBON, CLIMATE RESILIENT FUTURE: SECURE, CLEAN AND EFFICIENT ENERGY) under Grant Agreement No 101 006 744. The content presented in this document represents the views of the authors, and the European Commission has no liability in respect of the content. The Tianjin colleagues thank the financial support from the National Natural Science Foundation of China under grant numbers: 21 808 163 and 21 690 083. Y.S. Sang would like to express his gratitude to the China Scholarship Council for a visiting research within the EU-101 006 744 project.

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