Mechanism of Preparation of Platform Compounds from Lignocellulosic Biomass Liquefaction Catalyzed by Bronsted Acid: A Review

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Received 10 May 2019; Accepted 30 June 2019

Abstract: Over the past two decades, research on transforming lignocellulosic biomass into small molecule chemicals by using catalytic liquefaction has made great progress. Notably, in recent years it has been found the production of small molecule chemicals through directional liquefaction of lignocellulosic biomass. Understanding the liquefaction mechanism of lignocellulosic biomass is highly important. In this review, the liquefaction mechanism of lignocellulosic biomass and model compounds of cellulose are described, and some problems and suggestions to address them are described.

Keywords: lignocellulosic biomass; liquefaction product; platform chemical; bronsted acid; liquefaction mechanism

1 Introduction
Biomass resources are the only widely existing renewable resources except for coal, oil, natural gas and other fossil resources. Lignocellulosic biomass, the main existing form of biomass resources, can be divided into two categories: agricultural residues and forestry residues, including crop straw, fruit shells, economic forestry products, waste wood and wood-processing waste. Lignocellulosic biomass is essentially a complex material consisting of three types of oxygen-containing organic macromolecule polymers: cellulose (polymer of glucose), hemicellulose (heteropolymer of pentose, such as xylose and a small amount of hexacarbose) and lignin (amorphous aromatic macromolecule). Typically, lignocellulosic biomass contains 30%–50% cellulose, 20%–35% hemicellulose and 15%–30% lignin. China has abundant lignocellulosic resources, averaging approximately 900 million tons of tree branches and forest waste and 700 million tons of crop straw, which account for approximately 800 million tons of standard coal each year. Therefore, the preparation of high value-added products and liquid fuels from lignocellulosic biomass materials have great potential for development (Collard and Blin, 2014; Deng et al., 2015).

In general, according to product morphology and development status, the conversion and utilization technologies of biomass energy can be divided into three categories (Fig. 1): 1) biomass directly burned for heat energy or power generation; 2) biomass fermented or pyrolysis gasified to obtain methane or syngas; and 3) biomass liquefied to produce biomass-based liquid fuels (e.g., bio-oil, bio-ethanol and bio-diesel) through various liquefaction and other thermochemistry conversion technologies. After decades of continuous development, these technologies have been industrialized. Currently, scientists are increasingly turning their attention to the preparation of small molecule platform compounds such as alkyl glycosides, 5-hydroxymethyl furfural, levulinic acid and its esters from lignocellulosic materials, to decrease the dependence on non-renewable resources such as oil and gas (Luo et al., 2013).

Liquefaction technology is widely used to convert solid lignocellulosic biomass into liquid, and it can be classified into two types of operation: indirect liquefaction and solvent liquefaction. Indirect liquefaction initially converts biomass or its liquefied products into syngas,
from which fuels such as alcohols and alkanes are subsequently synthesized. During solvent liquefaction, lignocellulosic biomass is directly liquefied into liquid products, generally by using proton solvents such as water, phenols, low-carbon alcohols, sulfolane or other ionic liquids. Compared with indirect liquefaction, solvent liquefaction has the advantages of mild reaction conditions, higher yield of liquefaction products and easier directional regulation of products and so on; thus, it has become one of the main methods of conversion and utilization of biomass resources, and has attracted extensive attention from many researchers (Mika et al., 2018). In solvent liquefaction, various lignocellulosic biomass materials can be effectively converted into some kinds of important platform compounds, such as furfural, 5-hydroxymethyl furfural, levulinic acid and its esters, \( \gamma \)-pentyllactone (Deng et al., 2009; Deng et al., 2010; Qi and Horváth, 2012), alkyl glycosides and phenols by using water, low-carbon monoalcohols/polyols, phenols, esters or organic acids as solvents in the presence of a Lewis acid, Bronsted acid or another bis-functional catalyst (Huber et al., 2006; Kang et al., 2013). Through continuous optimization of technological conditions, much attention has been focused on the preparation of platform compounds with higher yields, which requires understanding of the generation path of target products. Thus, studies on the liquefaction mechanism of lignocellulosic biomass are particularly important. The following aspects are summarized in this review: (1) research of the preparation of small molecule platform compounds from lignocellulosic materials through catalytic liquefaction under atmospheric pressure; (2) research progress on the liquefaction mechanism of platform compounds, such as alkyl glycosides, levoglucosone, furfural, levulinic acid and its esters, from lignocellulosic biomass catalyzed by Bronsted acid; (3) trends in the development of catalytic liquefaction of lignocellulosic materials, as well as possible solutions to existing problems.

1. Structure and composition of lignocellulosic biomass

1.1 Structure of cellulose

Cellulose is the most widely present and abundant polysaccharide in nature and is commonly found in the cell walls of higher plants. In general, cellulose accounts for 40%–50% of tree wood. As shown in Fig. 2(1), it is a linear polymer composed of D-glucose linked by \( \beta \)-(1-4)-glycosidic bonds. Cellulose can be expressed by the molecular formula \((C_6H_{12}O_6)_n\), where \(n\) is the degree of polymerization, ranging from thousands to tens of thousands. The D-glucose is produced by complete hydrolysis of cellulose, and cellobiose \([\beta-D\text{-glucosyl}(1,4)-\beta-D\text{-glucoside}]\) and cellotriose are products generated from partially hydrolyzed cellulose. Because of the presence of multiple hydroxyl groups in glucose, hydrogen bonds are readily formed between the polymer chains; consequently, the molecular chains tend to aggregate into crystalline fibrillar structures.

1.1.2 Structure of hemicellulose

Unlike cellulose, hemicellulose possesses a more complex structure comprising a heterogeneous polysaccharide composed of units of five carbon monosaccharides (D-xylose and D-arabinose) and other six-carbon monosaccharides (D-mannose, D-galactose and D-glucose). The basic molecular formula of hemicellulose is \((C_5H_8O_4)_n\). It generally accounts for 10%–30% (wt) of wood. In contrast to cellulose, with its highly organized chain structure, hemicellulose has a branched-chain structure, and the degree of polymerization is only 50–200. Therefore, hemicellulose is easily decomposed and is...
mostly soluble in alkali solution. Figure 2(2) shows the structural formula of xylan hemicelluloses (a) and mannose hemicelluloses (b). The main chain of the former is composed of D-xylose linked by $\beta-(1\rightarrow4)$-glycoside bond, while the latter is composed of D-pyran mannose and D-pyran glucose linked by $\beta-(1\rightarrow4)$-glycosidic bond.

### 1.1.3 Structure of lignin

Lignin is a compound comprising a three-dimensional combination of phenylpropane and its derivatives, whose structure is complex and has not yet to be fully understood. Lignin monomers are a class of polyhydroxy compounds with a phenylpropene skeleton structure, including a p-hydroxyphenyl structure, guaiacol structure and syringyl structure (Fig. 2(3)). Lignin monomers form complex amorphous polymers through C—C bonds, C—O—C bonds or intramolecular/intermolecular hydrogen bonds of H—O—H. Lignin generally accounts for 20%–30% (wt) of wood.

# 2 Preparation of Small Molecular Platform Compounds Through Catalytic Liquefaction of Wood Fiber at Atmospheric Pressure

The catalytic liquefaction of cellulose under atmospheric pressure mainly uses Lewis acids (molecule, group or ionic acid that can accept foreign electron pairs), Bronsted acids (molecule, group or ion that can release protons), or certain alkali and ionic liquids as catalysts. And the different catalysts affect the liquefaction efficiency, liquefaction path and products distribution. In addition, a comparative analysis has indicated that both the Lewis acid and the Bronsted acid show better performance and have been more widely applied than alkali in catalytic liquefaction of lignocellulosic raw materials to prepare platform compounds (Kumar et al., 2015). Some studies have been conducted on the catalytic liquefaction of lignocellulosic biomass, and various liquefaction methods have been proposed to improve liquefaction yield (Isha et al., 2018) or to reveal related reaction kinetics and degradation mechanisms (Chang et al., 2006; Shi et al., 2016a; Shi et al., 2016b; Walker et al., 2018). In addition, the distinct structures of lignin, cellulose and hemicellulose result in different distributions of liquefaction products: the main liquefaction products of lignin are phenolic derivatives, whereas the counterparts of cellulose/hemicellulose are furfural and fatty acids and their derivatives (Fig. 3), thus making the separation and purification of liquefied products challenging (Capunitan...
To solve this problem, researchers usually use the following two methods: 1) raw materials with low lignin content (such as bamboo or corn cob) or low holocellulose (cellulose and hemicellulose) content (such as bagasse) are selected to be liquefied (Li et al., 2014; Liu et al., 2018); or 2) the three major components of lignocellulosic raw materials are separated before use (Liu et al., 2018; Jiang et al., 2018; Yang et al., 2018).

Many studies have reported methods for the separation of the three components of lignocellulosic raw materials and the efficient utilization of lignin (Ma et al., 2014; Rahimi et al., 2014; Shuai et al., 2016; Arni, 2018), but this paper mainly describes the efficient liquefaction of lignocellulosic raw materials and cellulose. In the liquefaction process, the main factors affecting product distribution are reaction time, temperature, pressure, catalyst and catalyst content, solvent and solvent content, among which the catalyst and solvent play prominent roles in the liquefaction process. Xu et al. (2010; 2012) have reported that methanol not only improved biomass conversion but also effectively prevented the further decomposition of liquefied products (sugar derivatives) into carbonyl compounds, thus enhancing the stability of the degradation products of cellulose and hemicellulose (sugar derivatives), and increasing the yield of products. Feng et al. (2015) have studied the effects of methanol and the dimethoxymethane/methanol composite solvent system on the liquefaction behavior of cellulose by changing the system of the liquefaction solvent, and the results showed that since dimethoxymethane/methanol composite solvent system has better protonation ability than methanol single solvent system, the platform compounds including methyl glycoside and levulinic acid ester could be prepared more efficiently. Ma et al. (2017) have analyzed the optimum liquefaction conditions for microcrystalline cellulose, xylose and bamboo by using response surface methodology. This study yielded a set of optimum technological parameters for bamboo powder: a ratio of 0.99꞉1 and 18꞉1 for phenol-solid and alcohol-solid, respectively, reaction time of 66.94 min, reaction temperature of 204.56°C and catalyst dosage of 5.09% (according to the mass fraction of bamboo powder). Under these conditions, the liquefaction rate of bamboo powder reached 99.902%. In the final experiment, when a 1꞉1 ratio of phenol to solid, 20꞉1 ratio of alcohol to solid and 5% dosage of catalyst were used, the actual conversion rate of bamboo powder reached 98.5%, and the yield of levulinic acid ester reached 65% after reaction of 60 min at 200°C.

Furthermore, Li et al. (2016) have found an increased content of heavy components in the liquefied products of straw cellulose with increasing methanol dosage in subcritical/supercritical methanol. Their further experiments on the influence of the hydrogen radical and hydroxyl radical on the distribution of liquefied products have revealed that increasing the content of free radicals in the reaction system resulted in a tendency of the light components in liquefied products to be polymerized to heavy components, thereby decreasing the liquefaction rate. The results of above studies showed that biomass liquefaction technology is an effective means of converting solid biomass into high value-added platform compounds and liquid products. And the types and dosages of solvents also play important roles in the distribution of liquefied products. Especially for inert solvents, their stability not only provides a favorable reaction medium but also prevents side effects. In addition, under the action of an acid catalyst on proton solvents with strong proton donor capacity, polymers such as cellulose and hemicellulose can be readily protonated in the initial stage of liquefaction, and open-chain depolymerization and open-ring reaction of depolymerized monomers subsequently occur (Isa et al., 2018; Mellmer et al., 2018).

We also summarized the parameters of the liquefaction process for several typical platform compounds, such as alkyl glycosides, furfural, 5-hydroxymethyl furfural, and levulinic acid and its esters, prepared from lignocellulosic biomass liquefaction (Table 1, Table 2 and Table 3). These data showed that, to some extent, the different catalysts could provide milder reaction conditions, and target chemicals could be prepared efficiently by using lower reaction temperature and less reaction time than before (Pileidis and Titirici, 2016). This phenomenon occurred during the preparation of either low-grade chemicals (e.g., alkyl glycosides) or high value-added

<table>
<thead>
<tr>
<th>No.</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>T (°C)</th>
<th>T (min)</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>α-cellulose</td>
<td>Ethanol</td>
<td>H2SO4</td>
<td>200</td>
<td>30</td>
<td>48.0</td>
<td>Zheng et al., 2018</td>
</tr>
<tr>
<td>2</td>
<td>α-cellulose</td>
<td>Ethanol</td>
<td>H4PW12O40</td>
<td>200</td>
<td>30</td>
<td>53.0</td>
<td>Zheng et al., 2018</td>
</tr>
<tr>
<td>3</td>
<td>Cellulose</td>
<td>Ethanol</td>
<td>Lig-SO3H H2O 17%</td>
<td>200</td>
<td>120</td>
<td>61.0</td>
<td>Zheng et al., 2018</td>
</tr>
<tr>
<td>4</td>
<td>Microcrystalline cellulose</td>
<td>Ethanol</td>
<td>H2SiW12O40</td>
<td>180</td>
<td>15</td>
<td>63.0</td>
<td>Deng et al., 2010</td>
</tr>
<tr>
<td>5</td>
<td>Bamboo</td>
<td>Methanol</td>
<td>H2SO4</td>
<td>200</td>
<td>10</td>
<td>40.6</td>
<td>Feng et al., 2015</td>
</tr>
<tr>
<td>6</td>
<td>Microcrystalline cellulose</td>
<td>Methanol</td>
<td>[Amin][Cl-H]PW12O40</td>
<td>170</td>
<td>165</td>
<td>70.2</td>
<td>Dora et al., 2012</td>
</tr>
</tbody>
</table>
Table 2  Preparation of furfural or 5-HMF (5-hydroxymethyl furfural) by catalytic liquefaction of lignin cellulosic

<table>
<thead>
<tr>
<th>No.</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>T (℃)</th>
<th>T (min)</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Grass</td>
<td>4 mL water-(0.35 g) NaCl/THF (1:3, V/V)</td>
<td>AlCl₃·6H₂O</td>
<td>180</td>
<td>30</td>
<td>66</td>
<td>Yu and Tsang, 2017</td>
</tr>
<tr>
<td>2</td>
<td>Maple wood</td>
<td>Water</td>
<td>H₂SO₄</td>
<td>170</td>
<td>40</td>
<td>62</td>
<td>Yu and Tsang, 2017</td>
</tr>
<tr>
<td>3</td>
<td>Microcrystalline cellulose</td>
<td>Ionic liquid</td>
<td>SPPS</td>
<td>140</td>
<td>240</td>
<td>68</td>
<td>Li et al., 2018</td>
</tr>
<tr>
<td>4</td>
<td>Cornstalk</td>
<td>Water-THF (1:4, V/V)</td>
<td>FeCl₃</td>
<td>170</td>
<td>80</td>
<td>42</td>
<td>Yu and Tsang, 2017</td>
</tr>
<tr>
<td>5</td>
<td>Barley shell</td>
<td>Water-DMSO (0.3:0.7)</td>
<td>Sulphani-licacid</td>
<td>150</td>
<td>60</td>
<td>41</td>
<td>Yu and Tsang, 2017</td>
</tr>
<tr>
<td>6</td>
<td>Maple wood</td>
<td>Water-THF (1:1, V/V)</td>
<td>FeCl₃</td>
<td>170</td>
<td>60</td>
<td>51</td>
<td>Yu and Tsang, 2017</td>
</tr>
</tbody>
</table>

Notes: ionic liquid, 1-methyl-3-ethyl imidazolium bromide; SPPS, heterogeneous sulfonated poly (phenylene sulfide); THF, tetrahydrofuran; DMSO, dimethyl sulfoxide.

Table 3  Preparation of levulinic acid/ethyl levulinate (LA/EL) by catalytic liquefaction of lignin cellulosic

<table>
<thead>
<tr>
<th>No.</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>T (℃)</th>
<th>T (min)</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cornstalk</td>
<td>Water</td>
<td>AlCl₃-NaCl</td>
<td>180</td>
<td>120</td>
<td>35.1</td>
<td>Zuo et al., 2014</td>
</tr>
<tr>
<td>2</td>
<td>Microcrystalline cellulose</td>
<td>Water</td>
<td>SA-SO₂H</td>
<td>180</td>
<td>720</td>
<td>51.5</td>
<td>Shen et al., 2017</td>
</tr>
<tr>
<td>3</td>
<td>Bamboo</td>
<td>Water</td>
<td>HCl</td>
<td>160</td>
<td>180</td>
<td>9.16</td>
<td>Sweygers et al., 2018</td>
</tr>
<tr>
<td>4</td>
<td>Microcrystalline cellulose</td>
<td>Water</td>
<td>Sulfated TiO₂</td>
<td>240</td>
<td>15</td>
<td>27.2</td>
<td>Wang et al., 2010</td>
</tr>
<tr>
<td>5</td>
<td>Pine wood</td>
<td>Ethanol</td>
<td>H₂SO₄</td>
<td>145</td>
<td>120</td>
<td>44.4</td>
<td>Li et al., 2014</td>
</tr>
<tr>
<td>6</td>
<td>Wheat straw</td>
<td>Ethanol</td>
<td>H₂SO₄</td>
<td>183</td>
<td>36</td>
<td>51.0</td>
<td>Tang et al., 2014</td>
</tr>
</tbody>
</table>

3  Mechanism of Atmospheric acid Catalytic Liquefaction of Cellulose

3.1  Mechanism of formation of cellulose liquefaction products

Different products are sourced from various lignocellulosic materials. For instance, products such as glycosides, levulinic acid, ethyl levulinate, lactic acid, furfuryl alcohol and furfural come from the degradation of cellulose and hemicellulose, whereas aromatic compounds (e.g., phenols) come from the decomposition of lignin. Various analytical methods have been developed for the identification of the liquefaction products (Staš et al., 2014), for which the formation pathways of several typical platform compounds (e.g., alkyl glycosides, furfural, 5-hydroxymethyl furfural, levulinic acid, propionate acetate and gamma-pentanolactone) have been discovered. However, there were two main research strategies on the mechanisms of formation of liquefied products: the first was the method using stable isotope labeling; the second was the quantum chemical method, for which density functional theory (DFT) was used to simulate the mechanism of formation of liquefied products (Yu and Tsang, 2017). These two methods required clear understanding of the composition of liquefied products and a preliminary understanding of the formation pathway of products. In contrast to the isotope labeling method, simulation required confirmation from supplemental experiments when the quantum chemical method was used. In addition, the quantum chemical method was best suited to studying pyrolysis mechanisms, whereas the influence of solvents on liquefaction mechanisms was difficult to evaluate.
levoglucosan (LG), and 5-hydroxymethyl furfural (5-HMF) is generally chosen to study the hydrolysis mechanism of the glycoside bond. Results of further studies showed that the liquefaction mechanism of cellulose is consistent with that of cellobiose and cellotriose. Zhang et al. (2014) have summarized the mechanism of preparing levoglucosan (LG) via cellulose pyrolysis and have suggested four kinds of mechanisms according to the reaction type: glycoside bond homocleavage reaction, glycoside bond heterolysis reaction, glucose intermediate formation reaction and synergistic reaction. Garcés et al. (2017) have studied the reaction mechanisms of formation of 5-hydroxymethyl furfural and levulinic acid from glucose and fructose catalyzed by hydrochloric acid. The results showed that further dehydration of glucose led to the formation of more by-products, such as dehydrated glucose and glucose oligomers. Patil and Lund (2011) studied the reaction kinetics of the formation of levulinic acid (LA) and formic acid catalyzed by 5-HMF protonic acid. The solid residues were characterized by scanning electron microscopy and infrared spectroscopy, thus indicating that the reaction of the formation of LA and formic acid was parallel to the process of humin formation, and the reactions compete with each other (Patil and Lund, 2011). Rasmussen et al. (2014) reviewed the reaction mechanism of the formation of small molecule platform compounds degraded from lignocellulosic biomass. They concluded that glucose could be converted into 5-HMF, levulinic acid, formic acid and different phenolic substances at high temperature, whereas xylose could form 2-furfural and various C-1 and C-4 compounds to according to different reaction mechanisms. Moreover, there are at least four ways to produce HMF from glucose and three ways to produce furfural from xylose. Choudhary et al. (2013) investigated the catalytic mechanism and reaction tendencies of glucose and fructose under the action of CrCl3 and HCl through fine structure diffraction via extended X-ray and molecular dynamics simulation, and the results showed that, as bifunctional group catalysts, Lewis acids significantly promoted keto-enol tautomerism, whereas the presence of a Bronsted acid inhibited the formation of CrCl3 into [Cr(OH)2]^+, thereby inhibiting the tautomerism reaction. Other researchers labeled carbon atoms in glucose and fructose through isotope labeling, then analyzed the mechanism of formation of 5-HMF and LA by C13-HMR (Akien et al., 2012; Qi et al., 2012; Zhang and Weitz, 2012; Yang et al., 2015). These data indicated that the carbon atoms in formic acid molecule originate from carbon 1 in the fructose and glucose molecules, whereas furfural could be produced from only fructose but not 5-HMF (Fig. 4). Thus, after the isomerization of glucose to fructose, a competitive reaction occurs in the further production of 5-HMF; that was, a portion of fructose undergoes ring opening, decarboxylation and dehydration to produce furfural (FF).

\[ \text{Glucose} \xrightarrow{\text{Isomerization}} \text{Fructose} \]

\[ \text{Aldose ring-opening} \]

\[ \text{Aldose-to-ketone tautomerization} \]

\[ \text{5-HMF} \]

\[ \text{Furfural (FF)} \]

\[ \text{LA} \]

\[ \text{HMF} \]

\[ \text{Formic acid} \]

\[ \text{No. 6 carbon} \]

\[ \text{No. 1 carbon} \]

**Fig. 4** Proposed schematic mechanism for acid catalytic conversion of glucose to furfural (FF), hydroxymethyl furfural (HMF) and then to levulinic and formic acids (Akien et al., 2012; Qi et al., 2012; Zhang and Weitz, 2012; Yang et al., 2015)

In addition, from the perspective of quantum mechanics, many studies worldwide have used DFT to investigate the mechanism of production of LG, LGO, 5-HMF and LA from cellulose pyrolysis, by using glucose, cellobiose, and cellotriose as model compounds (Zhang et al., 2013; Zhang et al., 2014; Yang et al., 2015; Zhang et al., 2016). Zhang et al. (2015) studied the initial mechanism of cellulose pyrolysis by using DFT with cellobiose as a model compound and found that several primary products, such as levogluconone, hydroxyacetic aldehyde and 5-hydroxymethyl furfural, were achieved through the depolymerization of cellulose chains, and a competitive reaction existed among the formation of these primary products. Zhang et al. (2013) studied the mechanism of LGO formation by cellobiose and LG, and the results indicated that LG was not likely to be the intermediate compound in the process of LGO formation. The researchers proposed that the formation of the LGO by either cellobiose or dextran was achieved through a 1,2-dehydration reaction, hexacyclic hydrogen transfer.
reaction and keto-enol tautomerization, and the keto-enol isomerization reaction was the rate-limiting step for the two other reactions. Wang et al. (2012) and Yang et al. (2012) studied cellulose pyrolysis through pyrolysis gas chromatography/mass spectrometry. The experiments classified products into three categories: pyran derivatives, furan derivatives and linear small molecule compounds. Through the DFT, the researchers also found that production of 5-hydroxymethyl furfural from glucan unit was easier than production of fufural from levoglucose units, and results were consistent with the experimental data. Using the DFT, Caratzoulas and Vlachos (2011) calculated more than 100 reaction pathways of production of 5-HMF and LA from glucose catalyzed by protonic acid (Fig. 5). When protonation first occurred on $O_2$ and $O_3$ respectively, formation of the LA is favored, while 5-HMF would be generated when protonated ring-opening first occurs on $O_5$. When $O_1$ and $O_2$ were protonated first respectively, glucose had a stronger tendency to produce humus through side reactions. Results from the above studies indicated that the difference in reactivity between glucose and fructose in acidic aqueous solution was mainly determined by the regioselectivity of the initial protonation step. In addition, the reaction products also showed large differences when the initial protonation sites differ. From the descriptions above combined with the experimental results, we summarized the well accepted two parts mechanism of cellulose liquefaction as follows.

![Fig. 5 An overview of possible conversion routes of glucose through protonation of different sites (Caratzoulas and Vlachos, 2011)](image)

3.2 Liquefaction mechanism of cellulose in proton solvents such as alcohols

3.2.1 Depolymerization mechanism of cellulose catalyzed by Bronsted acid

The comparison of the structures of alkyl glycosides, glucose and cellulose suggests that alkyl glycosides are the initial products of cellulose liquefaction, which can be obtained through continuous chain opening. Furthermore, the consensus from previous studies (Timell, 1964; Yamadaa and Ono, 1999; Hu et al., 2012; Xu et al., 2018) is that under the catalysis of a Bronsted acid, cellulose chains first open through two mechanisms: (1) closing-loop mechanism and (2) opening-loop mechanism, as
shown in Fig. 6. Regarding the closed-loop mechanism, oxygen in the 1,4'-glycoside bond reacts with acid catalysis to form electrophilic oxygen ions, and the glycoside bond breaks up to form a glycoside with the non-reducing end and a glycoside intermediate with oxonium ion ends under the sole electron attack of a nucleophilic epoxy. In terms of the opening mechanism, the protonation of the epoxy enhances the electrophilicity of C-1, and ring opening occurs when the C-1 is undergoes nucleophilic attack by hydroxyl (H/R-OH). Then proton transfer leads to a re-closed loop and breaks the glycoside bond, and glycoside with the hydroxyl/acetyl end of hemiacetal (which is called the reductive end) finally forms. As shown in Fig. 6, cellulose can produce two types of ends (alkyl glycosides) regardless of the pathway through which the cellulose chain opens (Lu et al., 2018; Lindstrom et al., 2019). In this process, the acidity of the catalyst strongly influences the reaction rate. Catalysts with stronger acidity can more easily provide protons, thereby enhancing the protonation of glycoside bonds and oxygen in epoxy and promoting the open-loop and closed-loop reactions, thus improving the degradation efficiency of cellulose.

3.2.2 Formation mechanism of levulinic acid (LA) and its esters

The alkyl glycosides and glucose obtained from cellulose open-chain depolymerization can gradually react with protonic acid to form monodehydrated pyran glucose, fructose, 5-HMF and its derivatives, and the LA and its derivatives (Fig. 2) (Horvat et al., 1985; Antal et al., 1990; Yamadaa and Ono, 1999; Lin, 2004; Grisel et al., 2014). In general, the formation of the LA from glucose or alkyl glucoside occurs through three steps: a dehydration reaction, keto-enol tautomerism and decarboxylation isomerization. The process of 5-HMF production involves two reaction pathways: 1) glucose dehydration produces monodehydrated pyran glucose, which in turn undergoes dehydration and isomerization to produce levoglucosone intermediates; and 2) alkyl glycosides are catalyzed by acid to produce glucose, which is then isomerized to produce fructose intermediates. In the last stage, the 5-HMF is hydrated to form 2,5-diketo-3-hexenal, and then the intermediate 5,5-dihydroxy-3-ene-2-pentanone (DPEO) is obtained by removing a molecule of formic acid catalyzed by protonic acid. The DPEO is further isomerized to intermediate a, levulinic acid and its esters. In addition, 4-hydroxycyclopentanone can also be obtained by acid-catalyzed cyclization of intermediate a (Amarasekara and Wiredu, 2015).

3.3 Liquefaction mechanism of cellulose in phenol

The first step of acid-catalyzed liquefaction of cellulose in phenol is the same as that in alcohols (Xu et al., 2018): cellulose is degraded in an acid-catalyzed reaction to form glucose and 5-HMF; the latter then reacts with solvent phenol to form phenol derivatives and other polymers. Lin (2004) detected 17 compounds by analyzing the liquefaction products of cellulose in phenol and divided them into four groups. The possible reaction path is shown in Fig. 8a. Group 1 compounds are three isomers of phenol and glucose, whose formation pathway may be protonation dehydration of C-1-OH in the D-glucose structure under the action of an acid to form a C-1 positive ion of dehydrated glucoside, then electrophilic reaction of the latter with phenol. The formation of Group 2 compounds is related to electrophilic substitution with phenol after the Group 1 compounds continue ring-opening via epoxy protonation, followed by the partial breakage of...
carbon bonds in the glucosyl group. Because the Group 3 compounds retain six carbon atoms in the structure of glucose, they may be obtained from Group 2-1 or Group 1 compounds through electrophilic substitution, protonation dehydration and cyclization with phenol. Group 4 compounds are generated from reaction with phenol after the carbon chain of Group 2-1 is protonated and fractured to form phenol alkyl carbon cations. Feng et al. (2011) characterized the liquefaction products of cellulose in phenol and found that the three compounds (1, 2, and 3 in Fig. 8b) can be obtained through nucleophilic substitution reaction of 5-hydroxymethyl furfural with phenol to varying degrees. In contrast to the liquefaction mechanism of cellulose in ethanol, phenol easily forms condensate with glucose, fructose, 5-HMF, LA and other intermediates, owing to its strong oxidation and high activity.

4 Conclusions and Prospects
The purpose of preparing small molecular chemicals and biodiesel from biomass liquefaction is to optimize the process conditions for industrialization, so that renewable resources (e.g., biomass) could make up for the disadvantages of non-renewable resources such as petroleum. The research on the conversion of biomass into fine chemicals by solvent liquefaction has made some progress, especially in the liquefaction of cellulose and lignin model compounds. The findings from this paper could help to understand the liquefaction mechanism of lignin biomass and be practically useful in the preparation, performed in recent years, of specific chemicals through directional liquefaction of biomass. However, the process of biomass liquefaction is complex and involves the destruction of hydrogen bonds among various molecules, the degradation of macromolecules and further reaction of the degradation products. Moreover, different reaction conditions affect the liquefaction yield, liquefaction products and liquefaction mechanism, thus hindering studies of the mechanisms. In addition, recent studies have mainly been
focused on improving the process conditions of catalytic liquefaction of biomass, however, little research has been performed to identify the structures of small and medium molecules in the liquefied products and the liquefaction mechanism. Therefore, some problems and suggestions for solvent liquefaction of lignocellulosic biomass are as follows.

(1) Because of the complexity of the composition of liquefied products, identifying the structures of small molecule compounds remains difficult, thus hindering the study of liquefaction mechanisms. As a result, such studies have remained at the stage of model compounds such as monosaccharides, and the reaction conditions are different from the actual liquefaction process. Therefore, developing new analytical methods for liquefaction products of wood biomass is particularly important. Liquefaction products have complex composition and low selectivity, thus resulting in low yield for single compounds. These products have poor usability and require a large workload including further separation and purification of single compound, thus increasing the industrial cost and even making industrial production difficult. To improve the conversion rate of single liquefied products, the mechanism of lignocellulosic biomass liquefaction should be understood, and, on this basis, by changing the process conditions of liquefaction, the directional liquefaction of lignocellulosic biomass was realized, further improved the conversion rate of biomass and the yield of single liquefaction product.

(2) At present, Bronsted acid catalysts (such as inorganic strong acids) exhibit excellent conversion efficiency and selectivity in the catalytic liquefaction of lignocellulosic biomass. However, industrialized production of these catalysts requires higher standards for equipment, and concentrated liquid acid catalysts are difficult to recycle and are likely to cause environmental pollution. Furthermore, current well performed reaction systems have some characteristics, such as higher reaction temperatures and longer reaction times. Therefore, to clarify the liquefaction mechanism, it is most important to explore novel, green, highly efficient catalysts and reaction systems with mild reaction conditions for lignin biomass liquefaction to prepare platform compounds.

(3) Although great progress has been made in the preparation of high value-added chemicals (e.g., 5-HMF, FF and LA) through catalytic liquefaction of model compounds such as glucose, fructose and xylose, the catalytic systems developed show high conversion efficiency and selectivity. Compared with simple Bronsted acid catalysts, specific Lewis acids and newly developed composite bifunctional catalysts display high conversion efficiency and selectivity. They also have outstanding performance in recovery and reuse, as compared with Bronsted acid catalysts, thus making gradual industrialization possible. However, given that glucose, fructose and xylose are all important platform compounds in the food industry, if industrialized production is realized, food competition, and even competition among people for food, might occur, thus resulting in a potential source of moral, ethical and social problems.

(4) In recent years, although great progress has been made in the directional preparation of high value-added chemicals through catalytic liquefaction of model compounds, breakthroughs still need to be made in choosing lignocellulosic materials for thermochemical conversion. The problems of low conversion efficiency and low selectivity of liquefied products should be addressed while taking production costs, environmental pollution and other factors into account. In addition, a breakthrough in large-scale laboratory research would be only the first step in understanding industrial production. On this basis, future studies should attempt to decrease the product losses caused by the purification of target compounds.

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