Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels

Chun-Hui Zhou,*a Xi Xia,a Chun-Xiang Lin,b Dong-Shen Tonga and Jorge Beltramini

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Lignocellulosic biomass is the most abundant and bio-renewable resource with great potential for sustainable production of chemicals and fuels. This critical review provides insights into the state-of-the-art accomplishments in the chemocatalytic technologies to generate fuels and value-added chemicals from lignocellulosic biomass, with an emphasis on its major component, cellulose. Catalytic hydrolysis, solvolysis, liquefaction, pyrolysis, gasification, hydrogenolysis and hydrogenation are the major processes presently studied. Regarding catalytic hydrolysis, the acid catalysts cover inorganic or organic acids and various solid acids such as sulfonated carbon, zeolites, heteropolyacids and oxides. Liquefaction and fast pyrolysis of cellulose are primarily conducted over catalysts with proper acidity/basicity. Gasification is typically conducted over supported noble metal catalysts. Reaction conditions, solvents and catalysts are the prime factors that affect the yield and composition of the target products. Most of processes yield a complex mixture, leading to problematic upgrading and separation. An emerging technique is to integrate hydrolysis, liquefaction or pyrolysis with hydrogenation over multifunctional solid catalysts to convert lignocellulosic biomass to value-added fine chemicals and bio-hydrocarbon fuels. And the promising catalysts might be supported transition metal catalysts and zeolite-related materials. There still exist technological barriers that need to be overcome (229 references).

1 Introduction

The depletion of fossil fuel resources and the resulting adverse effects on the global environment and climate are of major academic, economic and political concern worldwide.1–3 As supplies of fossil fuels and related petrochemicals may soon be limited, alternative solutions are sought. One alternative is to...
The weight percentage of cellulose, hemicelluloses and lignin in some typical biological sources: pine pinaster, eucalyptus globules, wheat straw, sorghum stalks, bamboo and banana pseudo-stems.

Fig. 1
and availability from bioresources and little impact on food supply, cellulosic materials as feedstocks are more practicable and sustainable for the production of fuels and commodity chemicals. In this context, the catalytic conversion of cellulose to fuels and chemicals is more attractive and promising than that of any other form of biomass like starch to bioethanol and vegetable oil to biodiesel.32–35

Still, lignocellulosic biomass such as wood, grass and agricultural residues are conventionally used as energy sources typically by direct combustion.36 The principal utilization of cellulose in industry is currently limited to textiles and paper manufacturing.37 In some biological processes such as fermentation and enzymatic catalysis, peculiar enzymes, bacteria and other microorganisms are used to break down cellulose molecules and thus a few commodity chemicals can be obtained.38,39 Nevertheless, such biological processes generally suffer from unsolvable problems such as low efficiencies, narrow reaction conditions and limited scale of production.39,40 Chemocatalytic conversion of cellulose has been around for some time, but it only receives serious attention in the advent of a series of novel chemocatalytic reaction routes since the fossil oil crisis in the 1970s.

However, besides the complexity of biological sources, the inert chemical structure and the compositional ratio of carbon, hydrogen and oxygen in molecules in lignocellulosic biomass produce additional difficulties in the chemocatalytic conversion of cellulose to valuable fuels and commodity chemicals. In this context, the development of a new family of highly active and selective catalyst systems is an essential prerequisite for chemoselectively catalytic conversion of lignocellulosic biomass to desired products.41 As such, this article attempts to summarize and review recent advancements in the different catalytic processes for the conversion of lignocellulosic biomass, in particular cellulose, into potential fuels and commodity chemicals.

Scheme 2 lists some typical fine chemicals and fuels which can be produced by chemocatalytic conversion of cellulose by different chemical processes. Clearly, a variety of fuels, including ethanol, hydrogen, methane and chemicals such as glucose, fructose, sorbitol, levulinic acid and lactic acid can be obtained from catalytic conversion of lignocellulosic biomass. Lignocellulosic biomass can also be used to produce syngas (\(\text{CO} + \text{H}_2\)) which can then be transformed into fuels and myriad chemicals.

In many instances, depolymerization and hydrolysis of cellulose to monomer glucose is regarded a necessary first step. Then glucose is further catalytically degraded into various intermediates, chemicals and fuels (Scheme 2, Route A). Recent research has paid much heed to accelerating the conversion of lignocellulosic biomass in the presence of multifunctional catalysts. The typical processes can be categorized as direct liquefaction, gasification and aqueous-phase reforming,
pyrolysis. An emerging trend is to integrate catalytically thermochemical conversion with selectively catalytic hydrogenolysis and hydrogenation with the addition of hydrogen.42–44 Because of the advantages of easy recovery and reusability of solid catalysts, heterogeneous processes have been taking priority over homogeneous catalytic processes. In addition, increasing endeavors are being made to integrate the two- or multi-step batch processes into a one-pass continuous conversion by using well-designed multifunctional catalysts with an expectation to transform lignocellulosic biomass into various commodity chemicals in an efficient and environmentally friendly way (Scheme 2, Route B).45

2 Catalytic hydrolysis of lignocellulosic biomass

Lignocellulosic biomass with cellulose as a main component is generally resistant to hydrolysis in water. As such, the hydrolysis of cellulose in lignocellulosic biomass usually involves the use of strong liquid acids as catalysts. Cellulose hydrolysis in the presence of acids primarily yields reducing sugars, which are a class of compounds that have an open chain with an aldehyde or a ketone group. Typically, glucose and xylose are obtained. Interests in such acid-catalyzed hydrolysis have been reignited because many fine and even platform chemicals can be obtained from further conversion of reducing sugars. Moreover, using a multistep fractionation process, various fine chemicals and potential fuels can also be directly obtained from acid processing of lignocellulosic biomass.46 Nevertheless, instead of the traditional use of liquid acids, nowadays much attention is given to the use of solid catalysts such as solid-supported Brønsted or Lewis acid reagent catalysts, acid-modified amorphous carbon, layered transition metal oxides, and acidic resins for the depolymerization of lignocellulosic biomass by hydrolysis (Tables 1 and 2).

2.1 Liquid acid-catalyzed hydrolysis

Acid-catalyzed hydrolysis of cellulose is a reaction in which hydrogen cations (H+) and hydroxide anions (OH−) from the splitting of molecules of water react with polymeric cellulose molecules, thereby yielding hydrolytic products by depolymerization. The discovery of such an acid-catalyzed reaction of cellulose hydrolysis has a relatively long history.55–77 Commercial microcrystalline cellulose is just a slightly depolymerized
TABLE 1  Typical hydrolysis of lignocellulosic biomass or pure cellulose with H2O over liquid acid catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Feedstock</th>
<th>Reaction conditions</th>
<th>Typical products</th>
<th>Yield (%)</th>
<th>Researchers/Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2SO4 (0.175 wt%)</td>
<td>Wood chips</td>
<td>483 K, 2 min &gt; 1.9 MPa</td>
<td>Xylose</td>
<td>47.0–54.0</td>
<td>Emmel et al./2003</td>
<td>57</td>
</tr>
<tr>
<td>H2SO4 (0.05 wt%)</td>
<td>Filter paper</td>
<td>488 K, 35 min 4 MPa (H2O)</td>
<td>Reducing sugar</td>
<td>46.6</td>
<td>Zhuang et al./2006</td>
<td>53</td>
</tr>
<tr>
<td>H2SO4 (0.1 wt%)</td>
<td>Cotton</td>
<td>473 K, 6 min 0.1 MPa</td>
<td>Levogluconesone Furfural 5-HMF</td>
<td>42.2 26.9 8.8</td>
<td>Kawamoto et al./2007</td>
<td>144</td>
</tr>
<tr>
<td>H2SO4 (0.5 wt%)</td>
<td>Corn cobs</td>
<td>398 K, 165 min</td>
<td>Xylose</td>
<td>25.0</td>
<td>Rivas et al./2008</td>
<td>55</td>
</tr>
<tr>
<td>H2SO4 (6.2 wt%)</td>
<td>Sugar maple wood extract</td>
<td>368 K, 50 min 0.1MPa</td>
<td>Xylose Glucose Rhamnose Mannose Galactose</td>
<td>161.6 g L−1 13.3 g L−1 12.4 g L−1 12.9 g L−1</td>
<td>Hu et al./2010</td>
<td>56</td>
</tr>
<tr>
<td>SO2 impregnation</td>
<td>Aspen chips</td>
<td>478 K, 3 min 1.62 MPa (H2O)</td>
<td>Glucose Levulinic acid</td>
<td>37.0 (wt%) 10.3 (wt%)</td>
<td>De Bari et al./2007</td>
<td>58</td>
</tr>
<tr>
<td>HCl (5 wt%)</td>
<td>Walnut shells</td>
<td>523 K, &gt; 30 min 1.5–8.6 MPa (H2O)</td>
<td>Glucose</td>
<td>~90.0</td>
<td>Liu et al./2006</td>
<td>59</td>
</tr>
<tr>
<td>HCl (20 wt%)/ + [EMIM]Cl</td>
<td>Cellulose</td>
<td>378 K, 2–4 h</td>
<td>Glucose HMF</td>
<td>~5.70</td>
<td>Binder et al./2010</td>
<td>68</td>
</tr>
<tr>
<td>CO2 + H2O (100% saturation)</td>
<td>Cellulose</td>
<td>533 K, ~2 min 20–25 MPa CO2</td>
<td>Glucose</td>
<td>~11.0</td>
<td>Rogalski et al./2008</td>
<td>64</td>
</tr>
<tr>
<td>ρ-toluenesulfonic acid + C4MIMCl</td>
<td>Cellulose</td>
<td>373 K, 5 h</td>
<td>Reducing sugar</td>
<td>35.0</td>
<td>Rinaldi et al./2008</td>
<td>90</td>
</tr>
<tr>
<td>H3PO4 (10 wt%)</td>
<td>Potato peel</td>
<td>408 K, 6 min</td>
<td>Reducing sugar</td>
<td>82.5</td>
<td>Lenihan et al./2010</td>
<td>60</td>
</tr>
<tr>
<td>Oxalic(0.1M) + NaCl</td>
<td>Cellulose</td>
<td>403 K, 6 h 3 MPa CO2</td>
<td>Glucose</td>
<td>2.8–3.9</td>
<td>Vom Stein et al./2010</td>
<td>67</td>
</tr>
</tbody>
</table>


product of cellulose by liquid acid-catalyzed hydrolysis.47,48 More importantly, various products such as glucose, xylose, arabinose and cellobiose and oligosaccharides can be readily formed from liquid acid-catalyzed hydrolysis of cellulose (Scheme 3).

Both inorganic liquid mineral acids such as H2SO4 and HCl, and organic acids such as various carboxylic acids and ρ-toluenesulfonic acid can be used as catalysts for the hydrolysis of cellulose. Various types of lignocellulosic biomass, for example wood chips, sawdust, corn-cobs, and walnut shells, have been tentatively processed by the liquid acid-catalyzed hydrolysis (Table 1). However, it should be pointed out that the hydrolysis mainly occurred in the cellulosic components in these lignocellulosic sources with glucose and xylose as the main products in most cases.

As summarized in Table 1, thus far H2SO4 has been the most frequently used liquid acid catalyst in the hydrolysis of lignocellulosic biomass. The reaction is usually conducted at temperatures in the range of 363–533 K and under atmospheric or higher pressure. In general, when a dilute acid solution is used, higher temperature and longer reaction time are necessary.49 In turn, when the hydrolysis reaction of cellulose is conducted at low temperature and in a short reaction time, concentrated acid is favorable. The treatment of cellulose in a concentrated acid solution remarkably accelerates such biopolymer molecules to be depolymerized to monomers.50,51 Usually, the yield of reducing sugars increases with increasing acid concentration. However, the use of concentrated acid solutions could lead to a decrease of the yield of glucose and xylose due to further degradation. Consequently, there is a substantial increase in the amount of products of further degradation of glucose or xylose, for example 5-hydroxymethyl-2-furfural (5-HMF).52 In addition, taking into account the operation safety, equipment corrosion and waste disposal, dilute acid is preferable for use in the hydrolysis of cellulose.53 Furthermore, as for catalytic performances in the hydrolysis of lignocellulosic biomass with a high content of hemicelluloses, dilute acid could be more effective than concentrated acid.54

The deep insights into the effect of pressure on the conversion and distribution of products are scarcely reported. However, it has been revealed that under atmospheric pressure, catalytic hydrolysis of cellulose is also feasible with both hydrolytic and dehydrated products.56 Clearly, under atmospheric pressure, higher temperature, concentrated acid and longer residence time are favorable to effectively depolymerize and degrade lignocellulosic biomass.

The impregnation of lignocellulosic biomass with acid solution can lead to partial destruction of the cellulosic parts in lignocellulosic biomass. Thereby such a pretreatment can facilitate their further hydrolytic reaction. For example, Emmel and co-workers57 reported that the pretreatment of wood chips by impregnating them in 0.175 wt% H2SO4 led to the remarkable hydrolysis of hemicellulose after the dilute acid-catalyzed hydrolysis at 483 K for 2 min in steam. Thus a yield of xylose up to 70% of its theoretical yield was obtained in the water-soluble fraction. In this case, the pretreatment temperature was found to influence the yield of xylose. Interestingly, impregnation with gaseous SO2 proved to be more effective than H2SO4 since a higher yield of...
glucose could be obtained.\textsuperscript{58} It was suggested that the addition of SO\textsubscript{2} catalyst (0.9% w/w dry raw material) reduced the degree of polymerization of the cellulose by an average of 50%. In addition to the catalytic performances, another noteworthy feature is that SO\textsubscript{2} is less corrosive than the H\textsubscript{2}SO\textsubscript{4} solution.

In addition to reaction parameters such as temperature, pressure, time and the concentration of acids, the type of acid catalysts is also an influential parameter for the distribution of products in the catalytic hydrolysis of lignocellulosic biomass. For example, in the presence of HCl acid in the hydrolysis of walnut shells, the yield of levulinic acid could reach 12%.\textsuperscript{59} This result might indicate that HCl acid as a catalyst could promote further catalytic dehydration of hydrolytic compounds, thereby resulting in the remarkable generation of levulinic acid. Dilute phosphoric acid is also an alternative catalyst.\textsuperscript{60} In a phosphate buffer solution at pH 2, the hydrolysis and dissolution of Japanese red pine wood chips under subcritical water conditions yielded hydrolytic saccharides and such further dehydrated products as 5-HMF and furfural.\textsuperscript{61} It might indicate that the presence of phosphate buffer could play a pivotal role in deep degradation of such a lignocellulosic biomass. However, in the absence of a catalyst, water-soluble saccharides can also be directly produced from the hydrolysis of lignocellulosic biomass, for example sugi wood powder, in supercritical and subcritical water.\textsuperscript{62}

Despite the relatively high catalytic activity of H\textsubscript{2}SO\textsubscript{4}, HCl and H\textsubscript{3}PO\textsubscript{4} in the hydrolysis of cellulose materials, by and large their uses are still uneconomical because the process suffers from severe corrosion, costly separation and neutralization of waste acids. These problems could be significantly addressed provided that carbonic acid (H\textsubscript{2}CO\textsubscript{3}), present in the form of a solution of CO\textsubscript{2} in water, can be used as a catalyst.\textsuperscript{63,64} First of all, carbonic acid has little corrosive effect. Secondly, theoretically, it can be

### Table 2  Typical hydrolysis of cellulose with H\textsubscript{2}O over solid acid catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Feedstock</th>
<th>Reaction conditions</th>
<th>Typical products</th>
<th>Yield (%)</th>
<th>Researchers/Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-SO\textsubscript{2}H + COOH + OH</td>
<td>Cellulose</td>
<td>373 K, 3 h</td>
<td>Glucose (\beta-1,4\text{-glucan})</td>
<td>4.0\textsuperscript{a}</td>
<td>Suginuma et al./2008</td>
<td>82</td>
</tr>
<tr>
<td>AC-SO\textsubscript{2}H + COOH + OH</td>
<td>Cellulose</td>
<td>373 K, 3 h</td>
<td>Glucose (\beta-1,4\text{-glucan})</td>
<td>~8.1\textsuperscript{b}</td>
<td>Yamaguchi et al./2009</td>
<td>78</td>
</tr>
<tr>
<td>AC-SO\textsubscript{2}H</td>
<td>Cellulose</td>
<td>423 K, 24 h</td>
<td>Glucose (\beta-1,4\text{-glucan})</td>
<td>0.93</td>
<td>Onda et al./2008</td>
<td>79</td>
</tr>
<tr>
<td>AC-SO\textsubscript{2}H (Sulfonation (T = 523) K)</td>
<td>Cellulose</td>
<td>423 K, 24 h</td>
<td>Glucose</td>
<td>61.0</td>
<td>Pang et al./2010</td>
<td>83</td>
</tr>
<tr>
<td>BC-SO\textsubscript{2}H</td>
<td>Cellulose</td>
<td>MW (350 W), 373 K, 1 h</td>
<td>Glucose</td>
<td>19.8</td>
<td>Wu et al./2010</td>
<td>81</td>
</tr>
<tr>
<td>HN\textsubscript{3}Mo\textsubscript{6}O\textsubscript{24}</td>
<td>Cellulose</td>
<td>403 K, 12 h</td>
<td>Glucose</td>
<td>21.0</td>
<td>Takagaki et al./2008</td>
<td>88</td>
</tr>
<tr>
<td>H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}</td>
<td>Cellulose</td>
<td>453 K, 2 h</td>
<td>Glucose Methyl Glucosides</td>
<td>50.5</td>
<td>Tian et al./2010</td>
<td>86</td>
</tr>
<tr>
<td>H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}</td>
<td>Cellulose</td>
<td>(\leq 473) K, 0.5 h CH\textsubscript{3}OH 3 MPa</td>
<td>Glucose 5-HMF</td>
<td>62.3</td>
<td>Wang et al./2011</td>
<td>89</td>
</tr>
<tr>
<td>CrCl\textsubscript{3}/LiCl + [C\textsubscript{4}MIM][Cl]</td>
<td>Cellulose</td>
<td>433 K,10 min</td>
<td>5-HMF 9.0</td>
<td>Hegner et al./2010</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>Nafion/silica</td>
<td>Cellulose</td>
<td>463 K, 24 h</td>
<td>Glucose</td>
<td>2.0</td>
<td>Van de Vyver et al./2010</td>
<td>73</td>
</tr>
<tr>
<td>Sulfonated silica/carbon nanocomposites</td>
<td>Cellulose</td>
<td>423 K, 24 h</td>
<td>Glucose</td>
<td>50.0</td>
<td>Van de Vyver et al./2010</td>
<td>73</td>
</tr>
</tbody>
</table>

AC: Active carbon. BC: Biomass char. [C\textsubscript{4}MIM][Cl]: 1-butyl-3-methylimidazolium chloride. MW: Microwave-assisted.\textsuperscript{a} catalyst: 0.300 g; cellulose: 0.025 g; distilled water: 0.7 g.\textsuperscript{b} catalyst: 0.300 g; cellulose: 0.25 g; distilled water: 2.25 g.

### Scheme 3  Possible products from acid-catalyzed hydrolysis of cellulose.\textsuperscript{90} Adapted and reprinted with permission from ref. 90. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
easily removed by depressurization and thus it does not leave any waste acid catalysts after reaction. Therefore, such a carboxic acid-catalyzed process is environmentally friendly. Rogalinski et al.64 reported that for the hydrolysis of cellulose in subcritical water with pressurized CO2 at 533 K, the yield of glucose could be significantly increased by the acidification of CO2 compared with that in pure water. Moreover, the onset of the formation of glucose is shifted to a shorter residence time due to the faster cleavage of 1,4'-β-glycosidic bonds facilitated by carboxylic acid. As for the catalytic mechanism, CO2 is believed to promote the hydrolysis reaction of cellulose by the formation and then dissociation of carboxylic acid in water to give active H+ cations, which then attack and break 1,4'-β-glycosidic bonds in cellulose (eqn (1)).63,64

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \approx 2\text{H}^+ + \text{CO}_3^{2-} \quad (1)
\]

The avoidance of the use of strong liquid acids offers an alternative approach to develop a green acid-catalyzed process. However, the insolubility of cellulose is another big barrier that needs to be tackled. In this context, one possible solution is to choose a suitable solvent. For instance, Recently Lin et al.65 investigated the hydrolysis and degradation of cotton cellulose treated with 1.39% HCl acid either in water or in ethanol at 338 K for more than 1 h. A higher yield of hydrolytic products was obtained in ethanol (2.44–5.04%) than in water (1.12–1.50%). Moreover, the effect of the reaction temperature on the yield of hydrolytic products in ethanol was much greater than that in water. The phenomena could be ascribed to the fact that the solubilization of cellulose is enhanced by ethanol. This might well explain why cellulose was more easily deconstructed in ethanol than in water. The other alternative solution is to use a mixture of inorganic and organic acids as catalysts.66 It has been found that dicarboxylic acids, like oxalic and maleic acid, are able to catalytically depolymerize cellulose, producing oligomers and glucose.67 The third solution is to use ionic liquids as the solvent and/or as the catalyst. Recently Binder and Raines68 reported a much effective process, in which water was gradually added to a catalytic system consisting of chloride ion liquid and acid catalysts (1-ethyl-3-methylimidazolium chloride, [EMIM][Cl + H2SO4 or HCl]). This method led to a nearly 90% yield of glucose from cellulose and 70–80% yield of sugars from corn stover in a few hours. In comparison to other conventional solvents and organic acids, however, the high cost of ionic liquids and the problematic reusability might still hinder its scale-up to commercial use.

Finally, in the liquid acid-catalyzed hydrolysis, besides acidic catalysts, solvents and reaction variables, the source of lignocellulosic biomass is also an important factor. Obviously, the molecular composition and arrangements of cellulose, hemicellulose and lignin in the plant cell wall changes throughout the life of the plant. Moreover, they differ among plant species, among tissues of a single species and even among geographical regions of the plant. The differences of chain length and hydrogen bonding pattern between amorphous hemicellulose and crystalline cellulose, for example, greatly affected the distribution of glucose and oligomers in the liquid products after catalytic hydrolysis.69 In addition, even the size of biomass feedstock particles may also be one of the important parameters. These are also common points worth consideration in any other processes discussed below.

2.2 Solid acid-catalyzed hydrolysis

Compared with homogeneous catalysts, heterogeneous solid catalysts have several advantages. In particular, solid catalysts can be easily separated from the liquid mixture after the reaction, thereby allowing the possible reuse of catalysts, along with the minimization of corrosion. Moreover, solid acid catalysts have the potential to be easily applied to a continuous flow fixed-bed reactor. These merits have stimulated the research and development of recyclable solid acids as replacements for the unrecyclable liquid acid catalysts in the catalytic hydrolysis of lignocellulosic biomass.70–72

As such, several types of solid acids, such as Nafion, Amberlyst, -SO3H functionalized ammonium carbon or mesoporous silica, H-form zeolites like HZSM-5, heteropolyacids and even metal oxides (for example, γ-Al2O3) have been explored on their catalytic performances in the catalytic hydrolysis of lignocellulosic biomass.74,75 Over solid acid catalysts, the typical hydrolytic products like glucose and xylose were also obtained, together with other chemicals such as β,1,4-glucan, furfural, 5-HMF, and levulinic acid. Furthermore, solid surface supported Lewis acid catalysts, for example FeCl3 supported onto ammonium silica, can also catalyze the hydrolysis of cellulose to glucose and then to levulinic acid even under relatively mild conditions.76 However, in most cases, over solid catalysts the catalytic activity and the selectivity to the desired products are quite low. Therefore, a longer reaction time is needed to acquire the high yield of glucose (Table 2), compared with liquid acid catalysts (Table 1).

As shown in Scheme 4, a commonplace insight into the hydrolysis reaction is that it involves the splitting of the water molecule into hydrogen cations (H+) and hydroxide anions (OH−). In the presence of cellulose, the H+ attacks the oxygen atom in the 1,4'-β-glycosidic linkage. Thus the 1,4'-β-glycosidic linkage is broken to form a cyclic carbonium cation with a chair shape. This step is considered as the rate-determining step.77 Finally, glucose is formed by rapid ion transfer of OH− from the dissociation of water molecules to the glucose unit-based carbonium cation. According to such a reaction mechanism, that a solid acid catalyst and reaction conditions favor the splitting of water will favor the hydrolysis of cellulose. The splitting of a water molecule into hydrogen cations (H+) and hydroxide anions (OH−) and hydroxide anions (OH−) can be regarded as deprotonation. It was discovered that the catalytic activity of a catalyst in the hydrolysis of cellulose increases with a decrease in the deprotonation enthalpy (DPE) of water on the surface of the solid acid catalyst.75 These findings suggested that stronger Brønsted acidity is more favorable to the catalytic hydrolysis of cellulose. In addition, to some extent, an increase in the amount of water had a positive effect on the breakage of 1,4'-β-glycosidic bonds and intramolecular hydrogen bonds in
insoluble cellulose, thereby leading to more hydrolytic products. Clearly, the formation of glucose requires more water than the formation of β-1,4-glucan. Yamaguchi and co-workers revealed that the amount of water comparable to the solid catalyst weight could lead to a maximum yield of glucose in the heterogeneous catalytic hydrolysis reaction of cellulose.

On the one hand, the conditions conducive to splitting of water molecules are needed. On the other hand, the conditions should help to avoid deep degradation. Therefore, mildly hydrothermal conditions were found favorable to the production of glucose from the hydrolysis of cellulose over solid acid catalysts. Among a series of typical solid acid catalysts like H-form zeolite, sulfated zirconia, sulfonated activated carbon and Amberlyst polymer-based materials (Amberlyst, a commercially available sulfonated resin), as reported by Onda and co-workers, sulfonated activated carbon showed a remarkably high yield of 40.5% of glucose (Fig. 2). Over such sulfonated activated carbon catalysts, a selectivity of higher than 90% to glucose was obtained. The catalysts could act in a way similar to sulfonic acids containing the group –SO3H, which has fairly strong acidity. The remarkably catalytic properties can be ascribed to the strong acidity of –SO3H functional groups and the hydrophobic planes on the surfaces of such a catalyst, as well as its high hydrothermal stability. Such systematic evaluation of a series of catalysts provided valuable information and clues for the design and preparation of a class of effective solid acid catalyst for catalytic hydrolysis of cellulose by adjusting its surface acidity and hydrophilicity/hydrophobicity.

It is worth noting that lignocellulosic biomass itself can be made into carbon materials by carbonization. Bio-char or activated carbon from lignocellulosic biomass such as bamboo, wood, and coconut shells are well-documented catalyst supports. Microwave-assisted hydrolysis of cellulose in water over a sulfonated bio-char acid catalyst (BC-SO3H) even showed a much higher turnover number (TON, 1.33–1.73) compared to that in dilute H2SO4 solution (TON, 0.02). The results were likely due to the strong affinity to 1,4′-β-glycosidic bonds of cellulose on the surfaces of such catalysts, thereby accelerating the activation of cellulose molecules. Microwave irradiation could strengthen the collision of cellulose particles in the reaction system. In addition, the surface of carbon solids can be functionalized with several functional groups. For example, Suganuma et al. described that a modified amorphous carbon material can simultaneously bear –SO3H, –COOH, and –OH groups by means of partial carbonization of cellulose, followed by sulfonation of the resulting amorphous carbon (Fig. 3). This strategy of catalyst preparation could efficiently enhance the performance of catalysts. Over such a catalyst, for example, when the hydrolysis of microcrystalline cellulose was conducted in a Pyrex reactor (catalyst = 0.300 g; cellulose = 0.025 g; distilled water = 0.700 g) at 373 K for 3 h, the yield of glucose and β-1,4-glucan reached 4% and 64%, respectively. The yield of glucose was increased to 8.08% under the optimized conditions (catalyst = 0.300 g; cellulose = 0.25 g; distilled water = 2.25 g). The enhanced catalytic performance is attributed to the good ability of such a material with a multi-functional surface to adsorb β-1,4-glucan. This view might be partly supported by the result that sulfonated silica/carbon nanocomposites exhibited high performance in the selective hydrolysis of cellulose into glucose. In this case, the hybrid surface structure constituted interpenetrated silica and carbon components which can greatly facilitate the adsorption of β-1,4-glucan on the solid catalyst. More recently, it was suggested that elevating the temperature of sulfonation during the preparation of sulfonated carbon catalysts enhanced their catalytic properties in the hydrolysis of cellulose. No matter what methods were used, in essence, the presence of strong, accessible

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**Scheme 4** Schematic mechanism of breakage of 1,4′-β-glycosidic bonds and formation of glucose in the hydrolysis of cellulose.

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**Fig. 2** Catalytic hydrolysis of cellulose over various solid acid catalysts at 423 K. Reaction conditions: milled cellulose 45 mg, catalyst 50 mg, distilled water 5.0 mL, 24 h. Ref. 79–Reproduced by permission of the PCCP Owner Societies.
Bromsted acid sites on catalysts played a crucial role in the catalytic hydrolysis of cellulose.

In addition to the surface-grafted or supported solid acids, heteropolyacids such as tungstophosphoric acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{HNbMoO}_6$ can also be used as heterogeneous-like catalysts for the catalytic hydrolysis of cellulose. For the hydrolysis of cellulose samples, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Sn}_{0.75}\text{PW}_{12}\text{O}_{40}$ catalysts gave a higher yield of total reducing sugars than $\text{H}_2\text{SO}_4$. A 50.5% yield of glucose with a selectivity higher than 90% were achieved over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts at 453 K for 2 h with a mass ratio of 0.42 of cellulose to $\text{H}_3\text{PW}_{12}\text{O}_{40}$. Over a series of catalysts like $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and polyvalent transition metal salts of $\text{PW}_{12}\text{O}_{40}^\text{3-}$ ($\text{Ag}^{+}$, $\text{Ca}^{2+}$, $\text{Co}^{2+}$, $\text{Y}^{3+}$, $\text{Sn}^{4+}$, $\text{Sc}^{3+}$, $\text{Ru}^{3+}$, $\text{Fe}^{3+}$, $\text{Hf}^{4+}$, $\text{Ga}^{3+}$ and $\text{Al}^{3+}$), the highest reaction rates were observed for the catalysts with moderate Lewis acidity, such as $\text{Sn}^{4+}$ and $\text{Ru}^{3+}$-containing catalysts.

In addition, layered transition metal oxides, for example $\text{HNbMoO}_6$, have also been found to be a class of effectively solid acid catalyst for the hydrolysis of cellulosic materials to glucose.

A 21% of the yield of glucose was obtained over layered $\text{HNbMoO}_6$ catalysts, even higher than that over Amberlyst-15 (3.4%) under the same reaction conditions (Table 2). The peculiar layered structure might make facile the accessibility of saccharides into the interlayer gallery of $\text{HNbMoO}_6$, where the strong acidic sites are located. Notably, such a layered structure exhibited good properties of water tolerance, which is of particular importance in a hydrolysis reaction.

Nevertheless, in the case of solid acid catalysts, there is a significantly poorer solid–solid reaction contact between catalysts and lignocellulosic biomass as both lignocellulosic biomass and solid cannot be dissolved in water. As such, either the $\text{H}^+$ ions from solid Brønsted acids or the active sites from solid Lewis acid are difficult to access by reactants. Therefore, the 1,4'-β-glycosidic bonds suffer from difficulty to be activated, attacked and then opened. Consequently, it results in a low reaction activity. Moreover, in practice, there is another difficulty in the use of solid catalysts. To determine the true conversion of lignocellulosic biomass remains an essential task because it is not easy to separate unreacted cellulose from sticky residues and various insoluble products that might readily be adsorbed onto the solid acid catalysts. To tackle these challenges, integrating the use of ionic liquids for dissolving microcrystalline cellulose along with solid acids for catalytic splitting of cellulose into sugars may provide a possible solution. For example, Rinaldi et al. showed that the cellulose biopolymers were broken down into oligomers in the form of averaging ten glucose units catalyzed by Amberlyst catalysts in 1-butyl-3-methylimidazolium chloride ($\text{C}_6\text{MIMCl}$) ionic liquid after 5 h. It was postulated that the easy release of $\text{H}^+$ ions into the solvent, the high surface area and large pores in Amberlyst catalysts were probably crucial factors to enable the long cellulose chains to be approached and activated, thereby increasing the reactivity.

Furthermore, to further convert in situ hydrolytic glucose to value-added commodity chemicals in a one-pot reaction system is promising. So far the acidic solids have proved to be effective in many reactions in organic synthesis. For example, alkylation is also an acid-catalyzed reaction. After acidic resin Amberlyst catalyzed the hydrolysis of the 1,4'-β-glycosidic linkages in the cellulose polymeric chain to give glucose, such acid catalysts could further catalyzed the in situ alkylation of the hydroxyl groups at the C1 position of the glucose as an intermediate. Consequently, cellulose was directly converted into an environmentally friendly alkyl glycoside surfactant in a one pot transformation.

This state-of-the-art integration of consecutive reactions has also been demonstrated in a recent work by Ignatyev et al. that cellulose was fully converted into alkylglycosides under mild conditions in the $\text{C}_6\text{MIMCl}$ ionic liquid in the presence of an acidic catalyst. Primary alcohols like n-butanol and n-octanol were used as alkylating reagents. In the reaction with n-butanol, the yield of butylglucopyranoside isomers reached 86%. According to a well-established concept, the removal of intermediate glucose by such alkylation can facilitate chemical equilibrium to move forward, thereby leading to a higher conversion of cellulose.

### 3 Catalytic solvolysis of lignocellulosic biomass

Apart from organic ionic liquid, certain organic reagents can also physically and chemically modify cellulosic materials by means of solvolysis, thereby promoting the contact between cellulose molecules and surfaces of a solid acid catalyst. In this context, the organic molecules act both as the solvents and as the reactants. Consequently, they can significantly facilitate the catalytic conversion of lignocellulosic biomass over a solid catalyst. Clearly, there is a chemical interaction between the solvent and the solute lignocellulosic biomass. Therefore, the inherent properties of solvents have a significant effect on products distribution. Moreover, it is also possible that organic solvents react with intermediates, for example oligosaccharides or monomers, to yield secondary products. Deng et al. reported that for the conversion of cellulose, the use of methanol as a solvent led to the formation of methyl glucosides in the presence of dilute $\text{H}_2\text{SO}_4$, heteropolyacids or sulfonated solid acid catalysts under mild conditions ($\leq 473$ K). $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts gave the highest TON ($\sim 73$ in 0.5 h) to methyl glucosides. Additionally, methyl glucosides formed in methanol are more stable against further degradation than glucose in water. Recently, it was revealed that alcohol (methanol or ethanol) and water showed a synergistic effect on direct liquefaction of biomass.
The 50 wt% co-solvent of either methanol-water or ethanol-water was found to be an effective mixed solvent for the liquefaction of eastern white pine sawdust. Comparatively, the dissolution of lignin and hemicellulose is easier than that of cellulose owing to the abovementioned differences in their chemical structure. Therefore, the solvolysis and degradation of cellulose might be worth being emphasized in the catalytic solvolysis of lignocellulosic biomass. Yamada et al.16 conducted the acid-catalyzed solvolysis of cellulose using ethylene carbonate (EC) as an organic reagent and 97% H2SO4 as catalyst. In contrast with solvolysis by using polyethylene glycol (PEG), using EC as a solvolysis reagent lead to a faster reaction rate. It was suggested that cellulose with EC led first to the formation of glucosides, which then decomposed to form HMF derivatives or levulinic acid as intermediates.16 In particular, HMF could be either decomposed or polymerized to form an insoluble fraction of products. Thereby, to obtain a desired levulinic acid, how to control the formation of HMF derivatives might be a critical issue. The solvolysis of lignocellulosic biomass can even proceed in the absence of catalyst under hydrothermal conditions. The results showed that the solvent such as acetone, ethylene glycol and toluene have a profound effect on solvolytic product. In addition, solvolysis can also be used to deal with intermediates from depolymerization or degradation of lignocellulosic biomass, for example 5-HMF, and levulinic acid.16,96 Thereby it might be applied to acceleration of a catalytic solvolysis process mainly through the solvolysis of intermediates.

Recently, Liu et al.97 investigated microwave-assisted-assisted organosolvolysis by a pretreatment of recalcitrant softwood in aqueous glyceral with a series of organic and inorganic acids with different pKa values including sulfuric, hydrochloric acid, phosphoric, malonic, acetic, citric and lactic acids. It was found that the efficiency of pretreatment correlated linearly with the pKa of the acids except malonic and phosphoric acids. Noticeably, the organic acids, for example carboxylic acids, could act simultaneously as the solvent, the reactant and the catalyst. Moreover, organic acids can be possibly recovered and reused by distillation or extraction. In addition to common organic acids like the carboxylic acids and sulfonic acids, organic compounds bearing an –OH or –SH group might also have certain acidity. Thus specific organic compounds can be judiciously selected for both catalysis and solvolysis of lignocellulosic biomass. The method could provide an economical alternative route to the selective conversion of cellulose to small organic molecules.

4 Catalytically hydrothermal liquefaction of lignocellulosic biomass

As discussed above, over certain acid catalysts, longer reaction time, higher reaction temperature and pressure can readily lead to deep degradation and decomposition of glucose, xylose, arabinose and cellobiose and oligosaccharides which are yielded from the hydrolysis of lignocellulosic biomass. Thereby a liquid mixture product mainly consisting of C2–C6 organic compounds are obtained. In this respect, such a process is usually called the liquefaction of lignocellulosic materials instead. Clearly, the objective of the liquefaction of lignocellulosic materials is to produce low molecular-weight liquid products, instead of glucose and xylose by hydrolysis.100

The catalytic liquefaction of lignocellulosic biomass is generally performed in hydrothermal water similar to conditions for hydrolysis at the temperature of 393–653 K (Table 3). An obvious advantage of the hydrothermal liquefaction process is that it does not require the lignocellulosic biomass feedstock to be pre-dried. Different from catalytic hydrolysis, however, the liquefaction process of lignocellulosic biomass targets deep degradation and decomposition of glucose through dehydration, isomerization, decomposition and rearrangement, and so forth.101 The products are greatly changed when the type of catalyst is substantially changed. For example, over halide catalysts, as shown in Scheme 5, glucose, 5-HMF and furfural could respectively decompose to liquid products, such as levulinic acid, 5-HMF, furan and formic acid, in a parallel reaction.102 However, over alkaline catalysts bio-oils and phenolic compounds are dominantly produced (Table 3).

4.1 Hydrothermal liquefaction over halide and sulfate catalysts

Recent literature reports that catalytic liquefaction of lignocellulosic biomass was often carried out over sulfate, halide and oxide-based catalysts. Lewis acid catalysts could exhibit good catalytic properties in hydrothermal liquefaction of lignocellulosic biomass while catalytic hydrolysis is frequently conducted in the presence of Brønsted acid catalysts (Table 3). Several studies suggested, for example, that alkali and alkaline earth metal chlorides were not effective in the conversion of cellulose, while transition metal chlorides such as CrCl3, FeCl3, CuCl2 and AlCl3,105,106 including a pair of these metal chlorides (for example CuCl2 and CrCl3),107 exhibited high catalytic activity. In particular, CrCl3 was found to be highly active in the conversion of cellulose to levulinic acid, reaching a yield of 67 mol% after 180 min at 473 K with a catalyst dosage of 0.02 M and substrate concentration of 50 wt%.108 In particular, the use of ionic liquids such as [C4mim]Cl105,106 and [EMIM]Cl107 can effectively promote cellulose depolymerization, thereby quickening the hydrothermal liquefaction. Recently, a one-step process for the conversion of lignocellulosic biomass into valuable furanic compounds in ionic liquids over CrCl3 under microwave irradiation was reported.105 The results showed that CrCl3 could effectively catalytically convert lignocellulosic biomass into 5-HMF and furfural with yields up to 52% and 31%, respectively, within a few minutes without any pretreatment. It was postulated that CrCl3 in [C4mim]Cl might form complexes [CrCl3]n[C4mim]m. Thus, in the presence of ionic liquid, the 1,4-glucosidic bonds were weakened partially at the cellulose hydrolysis step under microwave irradiation (400 W) because of coordination with [CrCl3]n.109 As a result, it was more easily attacked by water to form glucose and oligomers (Scheme 6).106 This coordination then promoted rapid mutarotation of the β-glucopyranose anomer of glucose to the β-glucopyranose anomer of glucose through hydrogen bonds of chloride anions with the hydroxyl groups of glucose. The hemiacetal portion of β-glucopyranose with [CrCl4]+ then formed a Cr3+ enolate anion complex and
In comparison to a non-catalytic process, the addition of 400 ppm La/Al$_2$O$_3$ (0.34 wt%) Cellulose $573$ K, $120$ s Lactic acid $\sim 6.6$ Kong et al./2008 109

La$_2$O$_3$ (0.34 wt%) Cellulose $523$ K, $180$ s (in N$_2$) Glucose $5.8$ (wt%) 5-HMF $19.2$ (wt%) 5-HMF Leuvalinic acid $2.3$ (wt%) 5-HMF Acetic Acid $4.0$ (wt%) 5-HMF Malic Acid $8.0$ (wt%) 5-HMF Lactic Acid $\sim 9.5$ Kong et al./2008 109

La$_2$O$_3$ (3.6 wt%)+[C$_4$MIM]Cl Cellulose MW (400 W) $2$ min, $0.1$ MPa 5-HMF 62.0 Li et al./2009 106

CrCl$_3$ + [C$_4$MIM]Cl Pine wood MW (400 W) $3$ min, $0.1$ MPa 5-HMF 52.0 Zhang et al./2010 105

CuCl$_2$/CrCl$_2$ + EMIM][Cl Cellulose $393$ K, $8$ min 5-HMF 57.5 Su et al./2010 107

CrCl$_3$ (3.02 M) Cellulose $473$ K, $3$ h Levanilic acid 67.0 Peng et al./2011 104

K$_2$CO$_3$ (0.5 wt%) Cellulose $608$ K, $4.7$ s bio-oil N/a Kumar et al./2008 124

K$_2$CO$_3$ (1.0 M) Empty palm fruit bunch Corn stalk $543$ K, $20$ min $2$ MPa (H$_2$O) Phenolic compounds N/a Akhtar et al./2008 119

Na$_2$CO$_3$ (1.0 wt%) Corn stalk $647$ K, $25$ MPa (H$_2$O) bio-oil $47.2$ (wt%) Song et al./2004 123

Na$_2$CO$_3$ Corn stalks $653$ K, $16$–$20$ min $8$ MPa (H$_2$) Heavy oil $53.3$ Qian et al./2007 122

Ca(OH)$_2$ (0.0243 M) Sawdust $553$ K, $15$ min Oil $9.3$ (wt%) Karagoz et al./2004 115

KOH (0.5 M) Walnut shells $523$ K, $>30$ min, $1.5$–$8.6$ MPa Phenolic compounds N/a Liu et al./2006 59

Ba(OH)$_2$ or Rb$_2$CO$_3$ Lignin $573$ K, $1$ h $2$ MPa, H$_2$ Phenolic compounds and oils $\sim 53$ Tymchyshyn et al./2010 126

K$_2$CO$_3$ Waste biomass $673$ K, $10$ min $22.1$ MPa Phenolic compounds and oils $\sim 32^\circ + 30^\circ$ Tymchyshyn et al./2010 126

K$_2$CO$_3$ Waste biomass $673$ K, $10$ min $22.1$ MPa Oil $9$–$13$% Hammerschmidt et al./2011 125

[EMIM][Cl]: 1-ethyl-3-methylimidazolium chloride. [C$_4$MIM][Cl]: 1-n-butyl-3-methylimidazolium chloride. N/a: not available. MW: Microwave irradiation. $^a$ data from reaction without catalysts, and the sum is the data with addition of catalysts.

4.2 Hydrothermal liquefaction over alkaline catalysts

One of the important features of lignocellulosic biomass is that it mainly contains two types of biopolymers, namely cellulose polymer and lignin polymer. Relatively speaking, the former readily interacts with acid while the latter is apt to interact with alkali. Therefore, in the presence of alkaline catalysts, liquefaction of lignocellulosic biomass mainly leads to oil-like products, although this process is usually conducted thermally with alkali. In a sense, this process mimics the conversion of ancient plant material into the crude oil. So far, various carbonates like Na$_2$CO$_3$, K$_2$CO$_3$, and hydroxides such as KOH or Ca(OH)$_2$ as catalysts have been evaluated in the hydrothermal liquefaction for wood, agricultural and civic wastes such as sugar cane bagasse and corn stalk as sources of lignocellulosic biomass (Table 3). The so-called bio-oil product is actually a complicated liquid mixture with a wide range of compositions. It typically consists of glycoaldehyde dimers, 1,3-dihydroxyacetone dimers, anhydroglucose,
soluble polyols, 5-HMF, furfural, organic acids, phenolic compounds and even hydrocarbons. Therefore, an efficient hydrothermal liquefaction process of lignocellulosic biomass over alkaline catalysts offers remarkable potential for simultaneously producing biofuels and value-added chemicals by integrating it with proper separation and extraction techniques.

Clearly, the reaction temperature and time and the type of alkaline medium have a significant effect on the reaction rate and product distribution. As for the effect of temperature on the reaction rate and the product distribution, for example, earlier Minowa and co-workers showed that in the presence of 0.826 wt% Na\textsubscript{2}CO\textsubscript{3} under 3 MPa, the decomposition of cellulose started at a reaction temperature lower than 453 K. Only water-soluble products were obtained at temperatures below 533 K. The cellulose decomposed quickly at 533–573 K. Bio-oil was formed at temperatures above 533 K and its yield reached the highest values at 593–613 K.

Scheme 5  Main reaction pathways of degradation of major product, glucose, from cellulose hydrolysis over different catalysts. Adapted and reprinted with permission from ref. 90. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Adapted and reprinted from ref. 102, Copyright 2008, with permission from Elsevier.

Scheme 6  Direct conversion of cellulose to 5-HMF catalyzed with CrCl\textsubscript{3} in [C\textsubscript{4}MIM]Cl (n = 1–3). [C\textsubscript{4}MIM]Cl: 1-n-butyl-3-methylimidazolium chloride. Reprinted from ref. 106, Copyright 2009, with permission from Elsevier.
No cellulose remained after reaction at temperatures greater than 573 K. Later, Karagoz and colleagues\textsuperscript{114} used a 0.0243 M Ca(OH)$_2$ solution as a solvent instead of pure water in a liquefaction reaction of wood biomass. The results also revealed that increasing the reaction temperature increased the conversion of wood biomass and the total bio-oil yield. Maximum bio-oil yield was found to be 8.5 wt\% for a reaction at 553 K for 15 min. Regarding these findings, in general, an obvious reason is that decomposition temperature for cellulose and lignin is inherently different. Moreover, decomposition of cellulose tends to yield polyols, alcohols and carboxylic acids while decomposition of lignin principally leads to phenolic compounds.

However, at elevated temperatures or over longer reaction times, the occurrence of secondary reactions of bio-oil products is increased so much that the yield of the bio-oil decreases. In particular, for most of the lignocellulosic biomass treated at a temperature higher than 573 K a carbonization process tends to readily take place.\textsuperscript{116} The carbonization could be effectively avoided at lower reaction temperature in the presence of an appropriate catalyst. With regard to low-temperature catalytic hydrothermal treatment of wood biomass, several studies showed that the use of alkaline catalysts increased the formation of the compounds such as 4-methyl-2-methoxy-phenol, 4-ethyl-2-methoxy-phenol and benzenediol derivatives and decreased the solid residues, tar and biochar.\textsuperscript{117,118} The role of catalysts in directing product distribution is clearly proved by the observation that the furan derivatives obtained from the thermal run were not observed for the catalytic run. Moreover, the conversion and yield of liquid products decreases in the following order: K$_2$CO$_3$ > KOH > Na$_2$CO$_3$ > NaOH.\textsuperscript{117-119}

It is most likely that the decomposition of lignocellulosic biomass in water inhibits char formation. In particular, such a process is conducted under subcritical or supercritical water conditions. It is well-documented that near the critical point of water (647 K, 22.1 MPa), the ionic concentration ($K_w = [H^+] × [OH^-]$; $[H^+] = [OH^-]$) increases and water behaves as a weakly polar solvent. Therefore, subcritical and supercritical water conditions are often considered to be applied to the liquefaction of lignocellulosic biomass. Earlier, Demirbas\textsuperscript{120} found that the yield of bio-oil from catalytic supercritical fluid extraction of oriental beech reached 68.6\% at 573 K after 30 min in the presence of 20\% wt NaOH. However, there are also disadvantages in the use of subcritical or supercritical water. Typically, the equipment corrosion by caustic hydroxides is severely enhanced under subcritical and supercritical water conditions. Therefore, in this aspect, alkali and alkaline earth carbonate salts are favorable for use as catalysts. When cellulose liquefaction is carried out in the presence of Na$_2$CO$_3$ under subcritical water and at a reaction temperature of 623 K, bio-oil and gas were the main products, with little solid residue formed.\textsuperscript{121} Qian et al.\textsuperscript{122} reported that when woody biomass was liquefied at 653 K in the presence of Na$_2$CO$_3$ as a catalyst, a yield of 53.3\% of bio-oil, mainly composed of hydrocarbon, aldehyde, ketone, hydroxybenzene and ester, was obtained. However, Song et al.\textsuperscript{123} showed that in the case of isothermal liquefaction of corn stalks in water without a catalyst, the conversion was also very high, reaching 95.4 wt\% with a liquid yield of 77.6\% and gas production of 17.9\%. When 1.0 wt\% Na$_2$CO$_3$ was added as a catalyst, the conversion rate remained unchanged (95.7\%), but the catalytic reaction favored the yield of liquid products which increased to 88.0\% and the gas production decreased to 6.8\%. Moreover, in the presence of a catalyst, the bio-oil content in the liquid products sharply increased from 33.4 wt\% to 47.2 wt\%. Clearly, not only does the catalyst change the rate of the liquefaction reaction, but it can also change the direction of the liquefaction reaction towards different types of products.

The hydrothermal liquefaction is almost all conducted in a batch reactor. However, it can be carried out in a continuous flow reactor. For example, Kumar et al.\textsuperscript{124} revealed that when using K$_2$CO$_3$ as a catalyst in a continuous flow reactor, increasing the reaction temperature to the supercritical region, or increasing the reaction time, hydrolytic oligomers and monomers of cellulose samples were further degraded into glycolaldehyde dimer, 1,3-dihydroxyacetone dimer, anhydroglucose, 5-HMF, and furfural, thereby yielding bio-oils. To improve the selectivity to target compounds in the bio-oil, Hammerschmidt and co-workers\textsuperscript{125} recently described a continuous one-step process making use of two kinds of catalysts, a homogeneous K$_2$CO$_3$ catalyst and a heterogeneous ZrO$_2$ catalyst. Such combination of a homogeneous system with a heterogeneous system provides new ways to realize a more efficient continuous process.

It should be noted that thermal liquefaction in an aqueous solution might also undergo hydrolysis, pyrolysis and steam gasification, in particular in super- or subcritical water. Such complex reaction networks for cellulose decomposition in homogeneous and heterogeneous reaction conditions under subcritical water using Na$_2$CO$_3$ and Ni as catalysts and without catalysts, have been proposed by Fang and co-workers, as shown in Scheme 7.\textsuperscript{121} In the course of the reaction, dissolved compounds, for example part of cellulose, oligomers, glucose, levoglucosan and non-dissolved feedstock cellulose and compounds, might undergo different reaction mechanisms, thereby resulting in different intermediates and final products. At a high heating rate, a Na$_2$CO$_3$ catalyst resulted in more oil while a Ni catalyst produced more gas. The dissolved reaction paths in the homogeneous phase were homogeneously hydrolyzed to glucose and other soluble pyrolytic products (e.g., levoglucosan), which then further decomposed to acids, aldehydes, and alcohols of C$_3$-C$_5$. Part of the glucose degraded to furfurals and 5-HMF, which ultimately condensed to phenols and dehydrated to levulinic and formic acids. The non-dissolved reaction fraction in the heterogeneous phase possibly underwent pyrolysis to yield a mixture of hydrocarbons, aromatic derivatives and tar, randomly linked oligosaccharides, light volatiles and gases via dehydration, cracking and fission, and rearrangement of the sugar units. Even for single cellulose as a feedstock, the reaction mechanism is extraordinarily complicated. For lignocellulosic biomass, the presence of lignin and hemicellulose certainly make it much more perplexing.

Among the components in bio-oils, phenolic compounds are one type of typical, important product from the liquefaction of lignocellulosic biomass after treatment with alkali. It is well-documented that alkalis are exceptionally effective to extract and convert lignin lignocellulosic biomass. Liu et al.\textsuperscript{59} showed that
the products from the hydrothermal conversion of walnut shells catalyzed by 0.5 M KOH at 573 K were mainly phenol derivatives, especially the methoxy phenolic compounds. Clearly, these chemicals are readily derived from lignin. Owing to the inherent multicomponent plant cells, small amounts of cyclopentene derivatives and C_{12–18} fatty acids were also detected. Recently Tymchyshyn and colleagues described a series of direct liquefaction of lignocellulosic wastes like sawdust and cornstalks, and model biomass compounds like lignin and cellulose in hot-compressed water at temperatures from 523 to 623 K in the presence of 2 MPa H₂, with the addition of Ba(OH)₂ and Rb₂CO₃ catalysts. Significant quantities of phenolic compounds such as 2-methoxy-phenol, 4-ethyl-2-methoxyphenol, and 2,6-dimethoxy-phenol were obtained from the two lignocellulosic wastes and pure lignin. Yet the liquid products from cellulose contained essentially carboxylic acids and neutral compounds. Such experimental data evidently revealed that lignin and cellulose inherently tend to result in different categories of products. To bear this in mind is of much importance in designing and developing a catalytic system for hydrothermal liquefaction of lignocellulosic biomass to the target products based on different goals.

As discussed above, catalytically hydrothermal liquefaction of lignocellulosic biomass produces a very complex mixture of liquid products along with some gases and solid residues and tars. It makes the production of bio-oil from hydrothermal liquefaction of lignocellulosic biomass very uneconomical at present when compared to the costs of diesel or gasoline production from fossil oils. Scheme 8 shows the separation and extraction procedure proposed by Karagoz et al. It involves the complicated multistep extraction by several types of solvents. Moreover it needs inorganic acids for neutralization and the separation of water-soluble organic compounds in the water phase. Therefore, in addition to the technical need for the improvement of the activity and selectivity of catalysts, the novel technology for separation and extraction of downstream products from hydrothermal liquefaction of lignocellulosic biomass need to be developed. On the other hand, such complexity in products is a reflection of the complex reaction mechanism in catalytic liquefaction of lignocellulosic biomass. Thus far, researchers have not acquired in-depth understanding of the reaction mechanism yet. To disclose it certainly is conducive to developing such a process for the commercial use. Finally, generally speaking, hydrothermal liquefaction is relatively time-consuming and energy-intensive. In this context, comparatively, fast pyrolysis, as discussed below, is more promising.

5 Catalytic pyrolysis of lignocellulosic biomass

Pyrolysis of lignocellulosic biomass is generally a process of thermal chemical decomposition in the absence of oxygen to convert biomass into liquid products (bio-oils) together with some gases and solid chars. Such a thermolysis process simultaneously involves various reactions such as depolymerization, dehydration, decarboxylation, esterification, condensation, cyclization, and so forth. However, different from catalytic liquefaction at lower temperature in the aqueous phase, pyrolysis is usually conducted at temperatures greater than 773 K (Table 4). The liquid products are commonly referred to as pyrolysis oils, which have been identified as promising alternative renewable liquid fuels.
5.1 Fast pyrolysis mechanism

The fast pyrolysis reaction of lignocellulosic biomass undergoes a complex mechanism in oxygen-deficient conditions at high temperature, even though the reaction is conducted in an inert atmosphere. Therefore, presently the investigation into the mechanism could be simplified through the single use of cellulose or lignin in a non-catalytic system. As shown in Scheme 9, earlier Luo et al. proposed a fast pyrolysis model of cellulose in an inert nitrogen atmosphere. Hydroxyacetalddehyde and 1-hydroxy-2-propanone was thought to be produced from the decomposed fragments of activated cellulose by competing against levoglucosan formation. Meanwhile, the intermediate fragments might also decompose to yield gases (CO\(_2\)). At low temperature, activated cellulose would also directly decompose to produce char, CO\(_2\), and H\(_2\)O. A long residence time of intermediates like levoglucosan in the reactor could lead to the secondary cracking reaction, thereby leading to the formation of methanol, aldehyde, allyl alcohol, glyoxal, furfural, 5-HMF and gases.

Regarding the gas products, a possible mechanism for fast pyrolysis of cellulose in an inert gaseous atmosphere was proposed by Lanza and co-workers recently, with the following simplified decomposition sequence:

Cellulose \(\rightarrow\) Gm, H\(_2\)O

\[ \text{where Gm = short oligomers.} \]

\[ Gm, \ \text{H}_2\text{O} \rightarrow C_n, \ \text{CO}, \ \text{H}_2\text{O} \ (\leftrightarrow \text{CO}_2, \ \text{H}_2), \text{ with } n \leq 4 \]

\[ C_n \rightarrow \text{CH}_4 \]

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]

As depicted by the reaction paths in eqn (2)–(5), cellulose decomposes primarily to H\(_2\)O and short oligomers (Gm), which is then broken down to levoglucosan. The levoglucosan easily breaks down to mainly form CO, H\(_2\)O and hydrocarbons up to C\(_4\), along with minor CO\(_2\) and H\(_2\). In these sequential reactions, butadiene was identified as a key intermediate. The hydrocarbons undergo further thermal cracking reactions to yield CH\(_4\). The presence of H\(_2\)O steam and hydrocarbons results in a reforming reaction, finally leading to chemical equilibrium composition among syngas and CH\(_4\). According to this mechanism, H\(_2\) and CO can form in two different reaction routes in eqn (2) and (5), respectively. And the different pathways and rates in the formation of CO and H\(_2\) explain why the ratio of CO to H\(_2\) is not constant under different conditions, particularly at short residence time. Therefore, it could be reasonably deduced that a longer contact time is required if the aim is to produce syngas from the fast pyrolysis of cellulose.

Although all of the abovementioned mechanisms have proposed relatively simple reaction routes and identified key intermediates in the non-catalyst system, it is evident that fast pyrolysis involves a series of consecutive and parallel reactions competing against each other among liquid products and gaseous products. Nevertheless, as such reactions are frequently conducted either in the gas or liquid phase in the presence of homogenous and heterogeneous catalysts, the reaction mechanism might undergo far more complicated

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Scheme 8 Separation and extraction procedure. Reprinted with permission from ref. 117. Copyright 2005, with permission from Elsevier. WSH: Water soluble hydrocarbons (WSH and others in wt% = 100 – (oil1 + oil2 + oil3 + solid + gas). (Typical products in oil 1: 2-Furancarboxaldehyde, 2-Methoxy-phenol, 4-Methyl-phenol, 4-Hydroxy-3-methoxy-benzeneacetic acid, 2-Hydroxy-3-methyl-2-cyclopenten-1-one and Butylated hydroxytoluene; oil 2: 3-Methoxy-1-propene, 4-oxo-Pentanoic acid, 5-Ethylidihydro-2(3H)-furanone; oil 3: 2-Furancarboxaldehyde,2-Methoxy-phenol, 3-Methyl-phenol or 4-methyl-phenol, Eugenol, 4-Hydroxy-3-methoxy-benzeneaceticacid-methyl ester, 3-Acetyl-7,8-dimethoxy-2-methyl-1H-naptho[2,1-b]pyran-1-one.

Similar to the liquid products from thermal liquefaction, the pyrolysis oil is a complicated mixture of oxygenated and deoxygenated compounds, typically consisting of organic acids, aldehydes, ketones, esters, aromatic and phenolic derivatives, and even hydrocarbons. Accordingly, liquid pyrolysis oils are normally acidic and emulsion-like fluids containing both aqueous phases and phenolic phases. Thus it is imperative to further upgrade pyrolysis oil so as to get useful liquid hydrocarbon-like fuels and fuel additives.

Pyrolytic processing of lignocellulosic biomass can be roughly classified into steam pyrolysis, fast pyrolysis in the flow of an inert gas and vacuum pyrolysis. For all of these approaches, a major, common objective is to improve the selectivity of low molecular-weight substances with great potential as fuels. As seen in Table 4, fast pyrolysis has been the attractive subject of a lot of research over the past decade because it is proven to be two to three times more economical than liquefaction and gasification processes. Generally, four parameters play a pivotal role in the catalytic activity and selectivity of targeted pyrolysis oils. They are (1) the catalysts, (2) heating rate of lignocellulosic biomass, (3) residence time of reactants and the products inside the reactor, and (4) reaction temperature. In addition, the atmosphere in the reactor is influential. For example, if the pyrolysis is conducted in the presence of hydrogen, more hydrogenated products will be obtained. Such an integrated pyrolysis with hydrogenation process will be discussed in detail in Section 7.
steps and reaction networks. Furthermore, many intermediate products are more active than cellulose itself and polyols, thereby making the reaction more perplexing. Such complex reaction networks are still a puzzle and a barrier on the way to understanding and utilizing cellulose by pyrolysis conversion in a more efficient, economical way.

5.2 Catalytic fast pyrolysis

To increase the pyrolysis efficiency and the content of the target compounds in bio-oils, liquid acid such as H2SO4, hydrochloric acid, phosphoric acid and Lewis acids can be used as a specific pretreatment for pyrolysis of lignocellulosic biomass.141 For example, Dobele et al.142 reported that the pretreatment of pine wood sawdust and microcrystalline cellulose samples with phosphoric acid or iron(III) sulfate drastically increased the contents of levoglucosenone and levoglucosane in volatile products obtained by a subsequent fast pyrolysis (Table 4). These results were attributed to the catalysis of the cellulose depolymerization and dehydration in the presence of acids from the pretreatment. As for the use of iron ions, possibly the cleavage of glycoside bonds were catalyzed by iron oxihydroxide which formed during pretreatment of lignocellulosic biomass. As a result, such a pretreatment had a positive effect on the yield of 1,6-anhydrosaccharides. With regards to lignocellulosic biomass with a higher content of

### Table 4 Typical pyrolysis of lignocellulosic biomass in the presence or absence of catalysts

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Typical products</th>
<th>Yield (%)</th>
<th>Researchers/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood bark and Hardwood</td>
<td>No</td>
<td>Vacuum pyrolysis, 773 K</td>
<td>Paraffins, sterols, Fatty acid methyl esters</td>
<td>N/a</td>
<td>Garcia-Perez et al./2007 134</td>
</tr>
<tr>
<td>Cellulose</td>
<td>No</td>
<td>Flash pyrolysis, 1123–1473 K, 35–75 ms.</td>
<td>Soluble solids, Liquid product</td>
<td>20.0–45.9</td>
<td>Piskorz et al./2000 135</td>
</tr>
<tr>
<td>Soybean oil cake</td>
<td>No</td>
<td>Pyrolysis, 773 K</td>
<td>Liquid product</td>
<td>12.5-27.4</td>
<td>Karagoz/2009 136</td>
</tr>
<tr>
<td>Cellulose</td>
<td>No</td>
<td>Fast pyrolysis, 1173 K, ≥3 h</td>
<td>CO2, H2, CH4, hydrocarbons</td>
<td>N/a</td>
<td>Lanza et al./2009 138</td>
</tr>
<tr>
<td>Cellulose</td>
<td>0.1 wt% sulfuric or polyphosphoric acid</td>
<td>Pyrolysis in tetramethylene sulfone, 473 K, 6 min, Under N2 flow</td>
<td>Levoglucosenone, furfural, 5-HMF</td>
<td>42.2</td>
<td>Kawamoto et al./2007 144</td>
</tr>
<tr>
<td>Wood</td>
<td>Pretreated by 1 wt% phosphoric acid</td>
<td>Fast pyrolysis, 773 K Under He flow</td>
<td>Levoglucosane</td>
<td>36.6</td>
<td>Dobele et al./2005 142</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Pretreated by 1% phosphoric acid</td>
<td>Fast pyrolysis, 773 K Under He flow</td>
<td>Levoglucosane</td>
<td>14.1</td>
<td>Dobele et al./2005 142</td>
</tr>
<tr>
<td>Pine wood sawdust</td>
<td>NaOH</td>
<td>Fast pyrolysis, 773 K Microwave heating</td>
<td>Acetol, Furfural 2-furanmethanal</td>
<td>53.3</td>
<td>Chen et al./2008 146</td>
</tr>
<tr>
<td>Pine wood sawdust</td>
<td>Na2CO3</td>
<td>Fast pyrolysis, 773 K Microwave heating</td>
<td>Acetol, Furfural 2-furanmethanal</td>
<td>45.28</td>
<td>Chen et al./2008 146</td>
</tr>
<tr>
<td>Pine wood sawdust</td>
<td>Fe2(SO4)3</td>
<td>Fast pyrolysis, 773 K Microwave heating</td>
<td>Acetol, Furfural 2-furanmethanal</td>
<td>1.03</td>
<td>Chen et al./2008 146</td>
</tr>
<tr>
<td>Cellulose</td>
<td>ZSM-5</td>
<td>Fast Pyrolysis, 873 K, 240 s Under He flow</td>
<td>Aromatic compounds CO2-Hydrocarbons</td>
<td>31.1 (C%)</td>
<td>Carlson et al./2008 152</td>
</tr>
<tr>
<td>Pine sawdust</td>
<td>Ni-ZSM-5</td>
<td>Flash pyrolysis, 673–773 K, 50 ms, under N2 flow</td>
<td>Hydrocarbons Toluene</td>
<td>16</td>
<td>French et al./2009 151</td>
</tr>
</tbody>
</table>

n/a: no available. No. without catalyst.

Scheme 9 Modified model of fast pyrolysis of cellulose.137 Adapted and reprinted with permission from ref. 137. Copyright 2004 American Chemical Society.
lignin, higher concentration of phosphoric acid or iron(III) sulfate was needed for pretreatment. Clearly, directly employing catalysts in the fast pyrolysis of lignocellulosic biomass can remarkably improve the conversion and selectivity to targeted products. As for the catalytic fast pyrolysis of microcrystalline cellulose at 773–1073 K by on-line analysis of the pyrolysis vapors, Lu et al.\textsuperscript{143} revealed that SO\textsubscript{4}\textsuperscript{2−}/SnO\textsubscript{2} was the most effective catalyst to yield 5-methyl furfural. The selectivity was evidently changed with the change of catalyst support. For example, the SO\textsubscript{4}\textsuperscript{2−}/TiO\textsubscript{2} catalyst favored the formation of furfural, while SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} favored the formation of furan.\textsuperscript{143} In addition, it is noteworthy that the type of solvent used during the pyrolysis reaction also has a significant impact on the distribution of products. Kawamoto et al.\textsuperscript{144} depicted the catalytic pyrolysis of cellulose catalyzed by H\textsubscript{2}SO\textsubscript{4} in tetramethylene sulfone (C\textsubscript{4}H\textsubscript{8}O\textsubscript{2}S) and found that the yield of levoglucosanone, furfural, and 5-HMF reached up to 42.2%, 26.9%, and 8.8% (as mol% yield based on the glucose unit), respectively, at 473 K for 6 min.\textsuperscript{144} Remarkably, the cellulose pyrolysis in tetramethylene sulfone suffered so little from carbonization reactions that the residues obtained from pyrolysis in sulfolane were colorless. There, levoglucosan was identified as the major anhydromonosaccharide formed during the pyrolysis of cellulose.\textsuperscript{145} Tetramethylene sulfone is an aprotic polar solvent and it could dissolve anhydromonosaccharides, therefore it could prevent the polymerization and carbonization reaction. As such, cellulose completely decomposed into soluble products in tetramethylene sulfone.\textsuperscript{145} In contrast, pyrolysis under nitrogen or in dioctyl phthalate (a poor solvent for levoglucosan) produced brown/black solid residues. The findings indicated that the solvent is also influential in pyrolysis and it can be properly selected in view of promoting dissolution of lignocellulosic biomass and/or intermediates.

At present, the catalytic pyrolysis of lignocellulosic biomass is often conducted in the presence of acid or alkaline catalysts such as carbonates and hydroxides. Because the pyrolysis oils yield various organic acids, the presence of alkaline species in the reaction system has an important effect on the stability of bio-oil. Phosphates, sulfates and chlorides also have certain catalytic activity in the catalytic pyrolysis of lignocellulosic biomass. With regard to the catalytic fast pyrolysis of pine wood sawdust by microwave heating in a fluidized reactor, alkaline sodium compounds like NaOH, Na\textsubscript{2}CO\textsubscript{3} and Na\textsubscript{2}SiO\textsubscript{3} catalytically resulted in bio-oils rich in acetol, and to some extent favored H\textsubscript{2} formation while the use of the Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} catalyst favored the formation of furfural and 4-methyl-2-methoxy-phenol.\textsuperscript{146} In addition, phosphates, sulfates and chlorides could be used to replace corrosive alkaline catalysts or corresponding acid catalysts. Other than catalysis, diammnonium phosphate (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4} and diammmonium sulfate (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} could act as dehydrating agents upon heating during pyrolysis. Therefore, at reaction temperatures of about 650–750 K, a pretreatment of water-extracted fire wood by the impregnation in about 1% of (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4} or (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} solution before pyrolysis is able to increase the yields of levoglucosan, 5-methyl-2-furaldehyde and 2-acetylfluran in the range of 2–5%.\textsuperscript{147} Furthermore, alkali and alkaline earth metal chlorides have also been investigated as catalysts. Shimada and co-workers\textsuperscript{148} showed that the use of alkaline earth metal chlorides could substantially reduce the reaction temperature from 673 to 423 K.

Recently, the catalytic pyrolysis of lignocellulosic biomass over zeolites and supported solid catalysts have received serious attention. In particular, it is attractive to employ continuous fast pyrolysis of lignocellulosic biomass catalyzed by solid catalysts which has obvious advantages over the use of liquid acid catalysts in a batch reactor. More importantly, the most desired product from the catalytic pyrolysis of lignocellulosic biomass should be directed to hydrocarbons-containing pyrolysis oils with high yield, similar to petrol presently in use with easy storage and transportation. In response, recent advances have shown that hydrocarbons can indeed be produced in considerable quantities by fast pyrolysis of biomass over zeolite and mesoporous catalysts such as ZSM-5, Al-MCM-41.\textsuperscript{149} Such a catalytic fast pyrolysis demonstrated an optimistic prospect for direct production of high-octane pyrolysis oils from biomass for practical applications. For instance, Olazar et al.\textsuperscript{150} studied the fast pyrolysis of pine sawdust with ZSM-5 in a spouted-bed reactor using nitrogen as the carrier gas and observed a yield of aromatic compounds of 12% (carbon). By using a semi-continuous flow reactor with helium as carrier gas, French et al.\textsuperscript{151} revealed that lignocellulosic biomass could be pyrolyzed at temperatures ranging from 673 to 873 K with a catalyst-to-biomass ratio of 5–10 by weight over nickel, cobalt, iron, or gallium-substituted ZSM-5, leading to an approximately 16 wt% yield of hydrocarbons. Aromatic compounds like toluene\textsuperscript{151} and even gasoline-like products\textsuperscript{152} can be obtained in remarkable quantities even without using the hydrogen. However, over solid catalysts at high temperature, the cracking and deoxygenating activity might decrease with time because of the coke deposits formed on the solid catalyst.\textsuperscript{152} Finally, it should be noted that the distribution of the pyrolysis products such as charcoal, liquids and gaseous products are also strongly influenced by the physical and chemical characteristics of the raw materials of lignocellulosic biomass. Therefore, the cellululosic sources with adequate chemical composition should be selected for the specific desired product, together with the search for optimal reaction conditions and the catalysts. In this context, the growth and productivity, ecological influence and cost of plant sources of lignocellulosic biomass should be taken into consideration.

6 Catalytic gasification of lignocellulosic biomass

Gasification is usually referred to as a process of oxygen-deficient thermal decomposition of carbonaceous matter such as coal, petroleum, biofuel, or lignocellulosic biomass with a major objective to produce valuable gaseous products like hydrogen or syngas.\textsuperscript{153–155} In particular, the production of hydrogen, an environmentally clean fuel, from cellulose biomass gasification is of much interest to scientists and engineers. Through Fischer–Tropsch synthesis techniques, bio-syngas can also be converted into synthetic liquid fuels and classified as clean and renewable transportation fuels.\textsuperscript{156} In this context, gasification plus Fischer–Tropsch synthesis are denoted as indirect liquefaction processes of lignocellulosic biomass. Gasification of lignocellulosic biomass can also be
performed at high temperatures with a controlled amount of oxygen like catalytic partial oxidation.\textsuperscript{157} Provided that air is used, the resultant products will contain nitrogen, thereby leading to an additional problem of separation and purification. In many instances, gasification also produces small amounts of tar, mainly composed of highly condensed poly-aromatic hydrocarbons.\textsuperscript{158,159} To avoid such a problem and to increase the efficiency, biomass gasification in supercritical water is of growing scientific and technical interest.\textsuperscript{160–162} This so-called steam gasification of cellulose, can be described by the following reaction (eqn (6)).\textsuperscript{163–165}

\begin{equation}
0.59\text{C}_6\text{H}_{12}\text{O}_6 + 0.7\text{H}_2\text{O} \rightarrow 1.42\text{CH}_4 + 2.12\text{CO}_2 + 1.4\text{H}_2 \\
(6)
\end{equation}

Table 5 lists some typical reaction conditions and results in catalytic gasification of lignocellulosic biomass in the presence of steam. The possibly improved solubility of cellulosic materials in the supercritical water employed can greatly reduce mass-transfer limitation. In addition, it can prevent catalyst deactivation due to coke deposition by means of extracting the coke precursor from the catalyst surface in the supercritical water.\textsuperscript{166} Moreover, the use of supercritical water might improve the hydrolysis and saccharization of cellulose in extremely short residence times. Furthermore, Fushimi \textit{et al.} recently revealed that the evolutions of water-soluble tar and gaseous products (\text{CO}, \text{H}_2, \text{CH}_4 and \text{C}_2\text{H}_4) are significantly suppressed by the interaction between cellulose and lignin.\textsuperscript{167}

6.1 Gasification over supported noble metal catalysts

Supported Ru, Pt or Pd catalysts appear promising in the catalytic gasification of lignocellulosic biomass under supercritical conditions (Table 5). In addition, these catalysts are commonly active for hydrogenation. Therefore, the H\textsubscript{2} produced from gasification in turn might be a reactant for \textit{in situ} consecutive hydrogenation.

Various Ru-based catalysts such as RuO\textsubscript{2}, Ru/TiO\textsubscript{2} and Ru/C have been explored as catalysts in the catalytic gasification of lignocellulosic biomass. Earlier, Park \textit{et al.}\textsuperscript{169} reported the production of hydrogen from sewage disposals in supercritical water using RuO\textsubscript{2} as the catalyst. The reaction was more effective than conventional steam reforming to produce hydrogen. Izumizaki and co-workers\textsuperscript{170} chose RuO\textsubscript{2} as a catalyst for the production of hydrogen from biomass in supercritical water under argon atmosphere of 44 MPa at 723 K for 120 min. The amount of hydrogen in gaseous mixtures was 15.0% from cellulose, 14.1% from pulp, 21.0% from the mixture of cellulose and lignin, 16% from waste paper and 27% from paper sludge, respectively. RuO\textsubscript{2} evidently accelerated the thermal decomposition for cellulose and pulp. However, for lignin, the catalytic performance could be greatly suppressed because of the quick deactivation of the RuO\textsubscript{2} catalyst by coke and char formation.

A possible reaction model over such a RuO\textsubscript{2} catalyst is proposed as below.\textsuperscript{170}

\begin{align}
\text{RuO}_2 + \text{Org} & \rightarrow \text{Ru}^{2+} + \text{Org}^+ + 2\text{CO} \\
\text{Ru}^{2+} + 2\text{H}_2\text{O} & \rightarrow \text{RuO}_2 + 2\text{H}^+ + \text{H}_2
\end{align}

\text{Org}^+ refers to an intermediate from the decomposed lignocellulosic biomass. According to such a proposition, CO was formed through the cyclic oxidation-reduction reaction of RuO\textsubscript{2} with intermediate organics compounds (Org) and then hydrogen was generated from the reduction of water by Ru\textsuperscript{2+} (eqn (7) and (8)). The hydrogen and CO could reacted to form methane (eqn (9) and (10)).

\begin{align}
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \\
2\text{CO} + 2\text{H}_2 & \rightarrow \text{CH}_4 + \text{CO}_2
\end{align}

(9) (10)

According to this reaction mechanism, a higher hydrogen ratio in the product stream is subject to low methane formation. In this case, the desired catalyst is the one which can significantly enhance the overall conversion of lignocellulosic biomass whilst hindering reduced methane formation so that the yield of hydrogen can be increased. Osaka \textit{et al.}\textsuperscript{171} showed that the gasification of cellulose over Ru/TiO\textsubscript{2} in supercritical water conducted at 673 K for 15 min led to a high gas yield of 74.4 C\textsubscript{2} (calculation based on the carbon balance). Nevertheless, using the same reaction conditions without the presence of a catalyst, the gas yield and the water-soluble yield were 11.3 C\textsubscript{2} and 39.0 C\textsubscript{2}, respectively. In this case, it is reported that in the catalytic reaction no solid product was formed.

In addition to the use of supercritical water conditions, to tackle the insolubility of cellulosic materials in gasification, there are a few reports suggesting that the derivative of cellulose, carboxymethylcellulose (CMC) and acetyl cellulose, can be mixed with particulate biomass and water to form a uniform and stable viscous paste. Such a mixture can then be gasified in a continuous flow system more efficiently.\textsuperscript{172,173} Hao \textit{et al.}\textsuperscript{173} found that the 10 wt% cellulose or sawdust sample mixed with CMC (2–3 wt%) can be completely gasified in supercritical water at 773 K, 27 MPa and for 20 min residence time in the presence of a Ru/C catalyst. And the experimental results suggested the catalytic activities in the order as follows: Ru/C > Pd/C > nano-(CeZr)\textsubscript{2}O\textsubscript{2} > nano-CeO\textsubscript{2} > CeO\textsubscript{2}.

When acidic solid support, for example in a Pt/Al\textsubscript{2}O\textsubscript{3} catalyst, was used, the catalytic gasification of lignocellulosic biomass could consist of two main steps: (1) Al\textsubscript{2}O\textsubscript{3} with surface acidity could effectively act as a catalyst in the first step for the depolymerization of a lignocellulosic biomass feedstock, similar to acid-catalyzed hydrolysis. As mentioned previously, in supercritical water this depolymerization can also occur to some extent even without catalysts. (2) The next step is the gasification of water-soluble depolymerized products over Pt/Al\textsubscript{2}O\textsubscript{3} in a catalytic reactor, producing H\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} (eqn (11)).\textsuperscript{174,175} Similarly, in the case of Pt/C catalyst in conversion of cellulose into hydrogen by aqueous phase reforming process, it was proposed that this process might involve slow hydrolysis of cellulose to glucose which was catalyzed by the H\textsuperscript{+} reversibly formed in water during the reaction and followed by rapid reforming of glucose to H\textsubscript{2}.\textsuperscript{176}

\begin{equation}
\text{Cellulose} \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{3\text{H}_2\text{O}} \text{6nC}_3\text{H}_6\text{O}_3\text{(H}_2\text{O)} \xrightarrow{\text{6nC}_3\text{H}_6\text{O}_3\text{(H}_2\text{O)}} \\
(11)
\end{equation}

Gasification of cellulose by the reforming reaction with H\textsubscript{2}O under high temperature can be regarded as catalytic wet oxidation.\textsuperscript{103,177}
Rh catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactants</th>
<th>Reaction conditions</th>
<th>Typical products</th>
<th>Yield (%)</th>
<th>Researchers/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/TiO2 (2 wt%)</td>
<td>Cellulose + H2O</td>
<td>673 K, 15 min</td>
<td>CH4</td>
<td>44.0</td>
<td>Osada et al./2004</td>
</tr>
<tr>
<td>Ru/C (5 wt%)</td>
<td>Sawdust + H2O</td>
<td>773 K, 20 min</td>
<td>CH4</td>
<td>9.0</td>
<td>Hao et al./2005</td>
</tr>
<tr>
<td>RuO2</td>
<td>Cellulose + H2O</td>
<td>723 K, 2 h</td>
<td>CH4</td>
<td>32.1 (^b)</td>
<td>Izumizaki et al./2005</td>
</tr>
<tr>
<td>Pt/Al2O3 (5 wt%)</td>
<td>Cellulose + H2O</td>
<td>623 K, 30 min</td>
<td>CH4</td>
<td>9.2 (vol%)</td>
<td>Usui et al./2000</td>
</tr>
<tr>
<td>Pd/Al2O3 (5 wt%)</td>
<td>Cellulose + H2O</td>
<td>623 K, 3 h</td>
<td>CH4</td>
<td>42.3</td>
<td>Usui et al./2000</td>
</tr>
<tr>
<td>Rh catalysts</td>
<td>Cellulose + H2O</td>
<td>1106 K(^b), 60 ms</td>
<td>CH4</td>
<td>7.7 (vol%)</td>
<td>Dauenhauer et al./2007</td>
</tr>
<tr>
<td>Ni/SiO2–Al2O3 (50 wt%)</td>
<td>Cellulose + H2O</td>
<td>623 K, 30 min or 1 h</td>
<td>CO2 + H2 + CH4</td>
<td>88.1</td>
<td>Minowa et al./1999</td>
</tr>
<tr>
<td>Ni NP</td>
<td>Wood</td>
<td>973 K, in N2</td>
<td>H2-rich gas</td>
<td>N/a</td>
<td>Richardson et al./2010</td>
</tr>
<tr>
<td>—</td>
<td>Palm empty fruit bunch</td>
<td>1023–1063 K</td>
<td>Gas</td>
<td>1.76 m(^3) gas kg(^{-1}) biomass</td>
<td>Lahijani et al./2011</td>
</tr>
</tbody>
</table>

\(^a\) Temperature measured at 10 mm from the top of the catalytic bed. \(^b\) L/per 100 g feedstock. NP: nanoparticles.

Usui et al.\(^{178}\) studied how cellulose is gasified in hot-compressed water at 623 K in the presence of a series of supported catalysts (2 wt% loading) using Zr(OH)\(_4\), (CH\(_3\)COCH\(_3\))(CO–CH\(_3\))Fe, ferrocene, Ru\(_3\)(CO)\(_{12}\), (CH\(_3\)CO–CH\(_3\))Fe, NiC\(_2\)O\(_4\), NiO, Ni(OH)\(_2\), 2NiCO\(_3\)–3Ni(OH)\(_2\), Pt\(_3\), CuCO\(_3\)–Cu(OH)\(_2\), (CH\(_3\)CO–Cu)–Cu–H\(_2\)O, (CH\(_3\)CO–Cu)–Cu–H\(_2\)O, and Cu(OH)\(_2\)). Among these catalysts, after reaction for 3 h, 5 wt% Pd supported on Al\(_2\)O\(_3\) particularly showed the highest catalytic activity, leading to a yield of H\(_2\) at 42.3 vol% and CH\(_4\) at 7.7 vol%, respectively (Table 5). A possible two-step mechanism is also proposed. Namely, first the C\(_2–C_{10}\) unit aldehydes, ketones, and organic acids were formed from cellulose in hot compressed water and then these intermediates were catalytically decomposed to give gaseous products mainly consisting of H\(_2\), CH\(_4\), CO, and CO\(_2\). It is noteworthy that using transition metal complexes as catalysts for the gasification of cellulose, oil and char were mainly produced with few gaseous products.

Many studies have shown that the deactivation of a catalyst in gasification of lignocellulosic biomass is often related to the amount of coke deposition.\(^{179}\) In addition to catalyst deactivation, the formation of tar readily causes trouble in downstream equipment such as blocking and fouling. Therefore, a good catalyst should be multifunctional, including the conducive roles in further catalytic steam reforming tar to syngas and in the removal of the inactive biochar by catalytic combustion. For example, Miyazawa et al.\(^{180}\) demonstrated catalytic partial oxidation of tar over a multicomponent Rh/CeO\(_2\)/SiO\(_2\) catalyst for syngas production from lignocellulosic biomass. In addition, Asadullah and coworkers\(^{181}\) conducted a series of experiments on Rh-based catalysts for gasification of cellulose and found that the Rh loading of 1.2 \(\times\) 10\(^{-4}\) mol g\(^{-1}\) catalyst supported on CeO\(_2\) exhibited multiple functions during the gasification of microcrystalline cellulose. The Rh/CeO\(_2\) catalysts remarkably increased the conversion and inhibited the formation of methane, thereby enhancing the yields of CO and H\(_2\), compared to Ru/CeO\(_2\), Pd/CeO\(_2\), Ni/CeO\(_2\), Rh/Al\(_2\)O\(_3\), and Rh/TiO\(_2\). These studies suggested that Rh/CeO\(_2\) has great potential to be developed as a catalyst for complete gasification of cellulose.

Finally, in addition to the catalysts and reaction variables, the reactor also plays a role in gasification efficiency and product distribution.\(^{182–186}\) Kaewluan et al.\(^{187}\) depicted a bubbling fluidized bed gasifier having a high carbon conversion efficiency (97.3%) and gasification efficiency (80.2%) to syngas from rubber wood chip. Dauenhauer and co-workers\(^{188}\) reported millisecond reforming, by which cellulose particles can be converted extremely quickly into syngas on a hot Rh surface without detectable deactivation from carbon formation.

### 6.2 Gasification over non-noble metal catalysts

It is well-documented that Ni, Fe, Co, and Cu-based catalysts are effective for the water-gas shift reaction in which carbon monoxide reacts with water to form CO\(_2\) and hydrogen (eqn (12)).\(^{189}\) Therefore, when such kinds of solid catalysts exist in the gasification of cellulose in the presence of steam, the yield of hydrogen can be increased (eqn (13)), possibly following a model involving in the water–gas shift reaction (eqn (12)).

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (12)
\]

\[
\text{Cellulose} \xrightarrow{\text{decomposition}} \text{water-soluble products} \xrightarrow{\text{gasification}\ (\text{Ni})} \text{gases(H}_2 + \text{CO)} \quad (13)
\]

\[
\text{methanation}\ (\text{Ni}) \xrightarrow{} \text{gases(CH}_4 + \text{CO}_2)}
\]

However, the H\(_2\) is readily released from the liquid phase to the gas phase. As a result, the catalyst cannot be in contact with a large concentration of hydrogen. This might prevent the methanation reaction from occurrence although methanation is readily catalyzed by such types of catalysts (eqn (9) and (10)). Recently, Sinag et al.\(^{191}\) compared the effect of nano-sized and bulky ZnO and SnO\(_2\) on the water-gas shift reaction in gasification of cellulose. The results showed that at 573 K the water–gas shift reaction proceeded faster over ZnO catalysts than that over SnO\(_2\) catalysts. Therefore, a higher yield of hydrogen was obtained in the presence of ZnO.
The methanation reaction could be also suppressed under subcritical and supercritical conditions. Minowa et al.\textsuperscript{192} reported that cellulose was gasified to hydrogen-rich gas over a nickel catalyst supported on kieselguhr in hot-compressed water at around 623 K and 18 MPa (subcritical conditions). During gasification, the steam reforming reaction and methanation reaction both occurred. The gas phase equilibrium composition was 41–46 mol% CH\textsubscript{4}, 47–49 mol% CO\textsubscript{2} and 6–11 mol% H\textsubscript{2}. Recently, a series of catalysts such as nickel, iron, copper, zinc, zirconium, ruthenium and RANEY\textsuperscript{8} nickel slurry were evaluated by Resende and Savage in the gasification of cellulose and lignin in supercritical water.\textsuperscript{193} The results revealed that the metallic catalysts played a critical role in the formation of gaseous product and the selectivity. The yield of hydrogen gas could be increased to some degree over nickel or copper by optimizing catalyst loading and the catalyst surface area/biomass weight ratio. However, it is worth noting that, in addition to the active component in a catalyst, usually the acidity and basicity of a support is also an influential factor on product distribution and coke formation. Interestingly, Tasaka and co-workers disclosed that steam reforming of tar derived from cellulose gasification was efficiently catalyzed by 12 wt% Co/MgO catalyst at 873 K in a fluidized bed reactor. Over such a type of MgO supported catalysts, the conversion of tar was found to increase with the amount of Co loading.\textsuperscript{194,195} Those findings indicate that the efficiency of gasification of lignocellulosic biomass could be greatly enhanced by endowing the catalysts an additional function of \textit{in situ} removal of tar by catalytic steam reforming.

7 Integrated hydroprocessing

Because the dominant components in lignocellulosic biomass are oxygen-rich cellulose carbohydrates, the depolymerization and degradation of lignocellulosic biomass by catalytic hydrolysis, solvolysis, liquefaction and pyrolysis primarily leads to oxygenated molecules with carboxyl, keto, and/or hydroxyl groups. Therefore, to yield targeted value-added chemicals and liquid hydrocarbons as transportation fuels, most oxygenated molecules should be further deoxygenated along with the formation of new C–C bonds. In other words, an additional hydrogenation or hydroprocessing is needed.\textsuperscript{196} When hydrogen is present in the reaction system over multifunctional catalysts, the partial or thorough removal of oxygen from the oxygenated molecules and the formation of C–C bonds by hydrogenation and aldol condensation, alkylation, or ketonization could occur simultaneously or \textit{in situ} consecutively.\textsuperscript{197} In addition, the catalytic hydrogenolysis of the glucosic carbon–oxygen (C–O and C=O) bonds in cellulose and hemicelluloses and aromatic carbon–oxygen (C–O) bonds in lignin may also take place in the presence of hydrogen.\textsuperscript{198} Therefore, the technology of integrating hydroprocessing with hydrolysis, solvolysis, liquefaction and pyrolysis has increasingly received attention over the past decade. And it has shown great potential for the production of the commodity chemicals and fuels from lignocellulosic biomass.\textsuperscript{199}

In the context of catalytic hydrogenation, supported metal catalysts, for example Pt, Ru, Pd or Ni catalysts conventionally possess superior catalytic properties. Moreover, these supported metal catalysts have relatively large surface areas with well-dispersed active metal sites. In addition, metal-support interactions might significantly contribute to the activity, selectivity and stability of a catalyst. The introduction of metal ions to a catalyst support can also modulate the acidity/basicity on the surfaces, thereby possibly facilitating the degradation of lignocellulosic biomass and reducing carbon deposition by both the support and the active metal sites. Over these supported catalytic metal catalysts, the efficiency of converting lignocellulosic biomass into hydrogenated products can be greatly enhanced through complicated reaction networks consisting of dehydration, dehydrogenation, hydrogenation, isomerization, oligomerization, decarbonylation and decarboxylation, and so forth.

7.1 Integrated hydroprocessing to produce commodity chemicals

As summarized in Table 6, presently many researchers use cellulose as a model of lignocellulosic biomass for investigation of the integrated hydroprocessing with hydrosythesis to produce commodity chemicals. A typical method is the combination of supported Pt, Pd or Ru catalysts for hydrogenation with liquid acid catalysts for hydrosythesis. It offers a more efficient route to the conversion of cellulose in a one-pot process reaction in the aqueous phase to form C\textsubscript{4} to C\textsubscript{6} sugar alcohols, in particular sorbitol, mannitol, and even ethylene glycol (Scheme 10, Table 6). In particular, sorbitol can be transformed to fuels (hydrogen, light alkanes and liquid alkanes) by aqueous-phase reforming or to a number of high value-added chemicals by aqueous-phase hydrodeoxygenation.\textsuperscript{200}

The type of noble metal and support, the type of acid, acid concentration and reaction time significantly influence cellulose conversion, carbon efficiency and product distribution.\textsuperscript{201} Notably, the breakage of cellulose involves the cleavage of two types of C–O–C bonds: the 1,4-\beta-glycosidic bond connecting two adjacent glucose monomers and the C–O–C bond within the glucose ring. Scheme 11 illustrates that over a ruthenium nanocluster catalyst the cleavage of the 1,4-\beta-glycosidic bond at a different position will result in two different products.\textsuperscript{202} Cleavage at the C\textsubscript{1}–O bond (position a) leads to dehydrated sorbitol, while cleavage at the position b gives dehydroxylated glucose. Therefore, to design a catalyst for a precise C–O–C cleavage is much conducive to the selectivity of the desired product.

In addition, when noble metals are supported onto acidic solids, possibly there is no need for the use of liquid acid. For example, over Pt/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts, the surfaces of \gamma-Al\textsubscript{2}O\textsubscript{3} support have acidic sites, which can catalyze the hydrosythesis of cellulose to glucose, and then the C=O group in the glucose molecule can be catalytically reduced by H\textsubscript{2} over Pt species on the surface of \gamma-Al\textsubscript{2}O\textsubscript{3}, thereby leading to the formation of hydrogenated products like sorbitol or mannitol.\textsuperscript{203,204} Nevertheless, \gamma-Al\textsubscript{2}O\textsubscript{3} itself is not acidic enough to efficiently hydrosythesize cellulose.\textsuperscript{118} The additional acidity can be produced from the interaction between Pt/Al\textsubscript{2}O\textsubscript{3} and hydrogen.\textsuperscript{28} Under the reaction conditions H\textsubscript{2} may undergo heterolytic dissociative chemisorption of hydrogen on platinum atoms. Moreover, hydrogen molecules activated on the platinum surface are able
to exchange with protons of the hydroxy groups on the surface of support Al$_2$O$_3$. These resultant H$^+$ species can reversibly spill over onto the surface of the catalyst support. Consequently, more Bronsted acid sites formed on the support which can then catalyze the hydrolysis of cellulose to glucose, followed by metal-catalyzed hydrogenation. This is part of the reasons that the presence of Pt/γ-Al$_2$O$_3$ was found to significantly increase the initial rate of dissolution-conversion as well.

### Table 6 Integrated hydrolysis with hydroprocessing in the conversion of cellulose over supported catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactants</th>
<th>Reaction conditions</th>
<th>Main products</th>
<th>Yield (%)</th>
<th>Researchers/Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/HUSY (2.5 wt%)</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>463 K, 24 h 5 MPa (H$_2$)</td>
<td>Sorbitol</td>
<td>0.7</td>
<td>Fukuoka et al./2006</td>
<td>205</td>
</tr>
<tr>
<td>Ru/PVP (1 wt%)</td>
<td>Celllobiose + H$_2$O + H$_2$</td>
<td>393 K, 12 h 4 MPa (H$_2$)</td>
<td>Sorbitol</td>
<td>23.18</td>
<td>Yan et al./2006</td>
<td>202</td>
</tr>
<tr>
<td>Ru/C (4 wt%)</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>518 K, 30 min 6 MPa (H$_2$)</td>
<td>Hexitols</td>
<td>39.3</td>
<td>Luo et al./2007</td>
<td>206</td>
</tr>
<tr>
<td>Ru/C</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>498 K, 5 min 6 MPa (H$_2$) + CH$_3$OH</td>
<td>EG</td>
<td>15%</td>
<td>Deng et al./2010</td>
<td>211</td>
</tr>
<tr>
<td>H$<em>2$SiW$</em>{12}$O$_{40}$ and Ru/C catalysts</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>463 K 5 MPa (H$_2$)</td>
<td>Polyol</td>
<td>65</td>
<td>Geboers et al./2010</td>
<td>209</td>
</tr>
<tr>
<td>Pt/γ-Al$_2$O$_3$ (2.5 wt%)</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>463 K 5 MPa (H$_2$)</td>
<td>Sorbitol</td>
<td>27</td>
<td>Yan et al./2006</td>
<td>202</td>
</tr>
<tr>
<td>Pt/PVP (1 wt%)</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>463 K 5 MPa (H$_2$)</td>
<td>Mannitol</td>
<td>6</td>
<td>Fukuoka et al./2006</td>
<td>205</td>
</tr>
<tr>
<td>Pt/Al$_2$O$_3$ (2.5 wt%)</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>518 K 30 min 6 MPa (H$_2$)</td>
<td>Sorbitol</td>
<td>6.0</td>
<td>Ji et al./2008</td>
<td>214</td>
</tr>
<tr>
<td>Pt/γ-Al$_2$O$_3$</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>463 K 24 h 5 MPa (H$_2$)</td>
<td>Sorbitol</td>
<td>15</td>
<td>Jolle et al./2009</td>
<td>204</td>
</tr>
<tr>
<td>HRuCl(CO)(PPh$_3$)$_3$, Rh/C</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>423 K 48 h 3.5 MPa (H$_2$) + C$_4$MIMCl</td>
<td>Glucose</td>
<td>&lt;1</td>
<td>Ignatyev et al./2010</td>
<td>208</td>
</tr>
<tr>
<td>2%Ni–30%W$_2$C/AC</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>518 K 30 min 6 MPa (H$_2$)</td>
<td>Sorbitol</td>
<td>3.9</td>
<td>Ji et al./2008</td>
<td>214</td>
</tr>
<tr>
<td>Ni/carbon fiber</td>
<td>Cellulose + H$_2$O + H$_2$</td>
<td>463 K 24 h 5 MPa (H$_2$)</td>
<td>Sorbitol</td>
<td>50.0</td>
<td>de Vyver et al./2010</td>
<td>212</td>
</tr>
</tbody>
</table>


### Scheme 10 Catalytic conversion of cellulose into polyols by integrated hydrolysis and hydrogenation. Adapted and reprinted with permission from ref. 206. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Adapted and reprinted with permission from ref. 214. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
as the selectivity to polyols, especially sorbitol.\textsuperscript{203,204} Moreover, in most cases, the hydrolysis reaction could be a rate-determining step.\textsuperscript{203–207} Thus an efficient conversion of cellulose into polyols can be realized through a combination of hydrolysis and hydrogenation over such a class of bifunctional supported metal catalysts.

In addition to Pt/\gamma-Al2O3, on the surface of a carbon-supported Ru cluster (Ru/C) catalyst, H\textsuperscript{+} ions could also be reversibly formed \textit{in situ} in hot water, thereby resulting in both catalytic hydrolysis and instantaneous hydrogenation.\textsuperscript{205,206} Moreover, integrated depolymerization of cellulose and hydrogenation can be carried out using ionic liquid C4MIMCl as a solvent in the presence of hydrogen.\textsuperscript{207} For example, Ignatyev \textit{et al.}\textsuperscript{208} recently discovered that the combination of a heterogeneous metal catalyst and a homogeneous Ru catalyst proved to be effective in such a process in the ionic liquid, possibly because the Ru compound can enhance the transfer of hydrogen to the metallic surface.

In addition, heteropoly acids together with supported noble metal catalysts exhibit good performances in the conversion of lignocellulosic biomass into valuable platform chemicals via combined hydrolysis and hydrogenation.\textsuperscript{209} More recently, Palkovits \textit{et al.}\textsuperscript{210} showed that heteropoly acids together with supported Ru catalysts show not only high activity but also remarkable selectivity for sugar alcohols reaching up to 81\% yield of C\textsubscript{4} to C\textsubscript{6} sugar alcohols at 433 K for 7 h. Noticeably, over supported Ru catalysts in the presence of basic solution, an integrated one-pot conversion of cellulose could be developed to produce valuable specific polyols such as ethylene glycol (EG), 1,2-propanediol, and 1,2,5-pentanetriol.\textsuperscript{211}

Ni supported onto carbon is also an alternative catalyst for a one-pot process of catalytic cellulose to polyols.\textsuperscript{212} Interestingly, a series of bimetallic catalysts including Ru-W/AC, Ir-W/AC, Pd-W/AC, Pt-W/AC, Ni-W/SiC, and Ni-W/TiO\textsubscript{2} proved to be highly active and selective for the formation of EG from cellulose.\textsuperscript{213} W was considered as a key component for degradation of cellulose, namely, the C–C cracking reactions, while the transition metals were mainly responsible for the hydrogenation reactions of unsaturated intermediates. Recently, Ji \textit{et al.}\textsuperscript{214} demonstrated that supported tungsten carbide catalysts can replace supported noble metal-based catalysts to catalyze the degradation of cellulose. Moreover, the use of Ni-W\textsubscript{5}C/AC catalysts showed remarkable selectivity towards EG with a yield up to 61 wt\% after 30 min at 518 K and 6 MPa H\textsubscript{2}. In addition to integrated hydrolysis and hydrogenation, integrated aldol-condensation and hydrogenation of lignocellulosic biomass (corn cobs) to produce water-soluble C\textsubscript{5}–C\textsubscript{15} compounds was recently developed in a single reactor system over Pd/WO\textsubscript{3}–ZrO\textsubscript{2} catalysts.\textsuperscript{215} The promising progress means that there is still plenty of scope to design more efficient catalysts for the one-pot catalytic conversion of cellulose into value-added polyols and other fine chemicals.

7.2 Integrated hydroprocessing to produce fuels

Another major objective of integrating hydroprocessing is to convert lignocellulosic biomass to liquid hydrocarbons so that they can directly replace the present gasoline and diesel fuels in transportation applications. In this context, the processes of hydrogenating hydrolytic compounds and hydrogenating pyrolysis oil have been intensively investigated. Moreover, lignocellulosic biomass is used more often as a starting material, rather than pure cellulose model samples.

Studies have shown the possibilities for yielding diesel and gasoline from lignocellulosic biomass by integrated hydroprocessing with acid-catalyzed hydrolysis. Recently it was revealed, for example, that an integrated process can produce gasoline with high octane numbers from maple wood.\textsuperscript{216} Such a process involves dilute acid-catalyzed (H\textsubscript{2}SO\textsubscript{4}, oxalic acid) hydrolysis of maple wood into aqueous carbohydrate solutions at 433 K, followed by aqueous phase hydrodeoxygenation of the resulting sugar solutions. Thus it led to a product similar to gasoline with a carbon yield of up to 57\% and an estimated octane number of 96.5. Because of the complicated compositions of hydrolytic products, hydrodeoxygenation of aqueous carbohydrate stream was realized by a two-stage selectively catalytic process: first the catalyst bed contained a Ru/C catalyst at 393 K and the second catalyst bed contained a Pt/zirconium phosphate catalyst at 518 K. As discussed previously, pretreatment by organic solvent can be significantly helpful to dissolve or solvolyze lignin, cellulose or hemicellulose in lignocellulosic biomass. Clearly, it is also conducive to the integrated process of hydrolysis and hydrogenation. It was demonstrated that the pretreatment of cellulose in 1-hexanol at 623 K, followed by hydrocracking catalyzed by Pt/HZSM-5(23) at 673 K in the presence of hydrogen, produced C\textsubscript{2}–C\textsubscript{9} alkanes with a remarkable yield up to 89\%.\textsuperscript{217} Compounds other than hydrocarbons from lignocellulosic materials also have potential for use as fuels. For example, Lange and co-workers\textsuperscript{218} reported that over bifunctional
catalysts Pt/TiO2 and Pt/ZSM-5 valeric esters as biofuels were produced from lignocellulosic materials. The synthesis of valeric biofuels consisted of acid hydrolysis of lignocellulosic materials to levulinic acid, hydrogenation of the levulinic acid to g-valerolactone (gVL) and valeric acid (VA), and its subsequent esterification to valeric biofuels (Scheme 12A). According to the proposed mechanism for the conversion of gVL to VA over bifunctional catalysts (Scheme 12B), the optimal production of VA requires a balancing of the acidic and hydrogenation functionalities of the bifunctional metal/zeolite catalyst. Therefore, changing the ratio of metal to zeolite led to different intermediates and products. Low metal loading onto zeolite resulted in an increase in the coproduction of pentenoic acid. High metal loading favored the formation of methyl tetrahydrofuran (MTHF), pentanal/pentanol, and/or pentane/butane. In particular, it is noteworthy that valeric biofuels were found to be fully compatible for blending with gasoline or diesel. More recently, Serrano-Ruiz et al. described219,220 that the deconstruction of cellulose in an aqueous solution of H2SO4 yielded an equimolar mixture of levulinic acid and formic acid. The formic acid could then be decomposed into H2 and CO2 and thus H2 was consumed to reduce levulinic acid to GVL in the H2SO4 solution over a Ru/C catalyst. Moreover, the formation of GVL brought about easy separation and recycling of the used H2SO4 in the cellulose deconstruction reactor. Remarkably, in a single reactor by means of a dual catalyst bed of Pd/Nb2O5 and ceria-zirconia; levulinic acid and GVL could be catalytically upgraded to 5-nonanone and then liquid hydrocarbon fuels similar to diesel and gasoline.

In addition to hydrotreating hydrolytic products, hydrotreatment of the pyrolysis oil of lignocellulosic biomass is also a promising option for the production of C-H-rich fuels from lignocellulosic biomass. One example is the extraordinary finding by Vspute and co-workers documenting that the further hydrotreatment of the pyrolysis oil greatly increased its intrinsic hydrogen content, thereby leading to light olefins and aromatic hydrocarbons.221 Over zeolite catalyst, the yield of aromatic hydrocarbons and light olefins could be tuned through the amount of hydrogen added to the biomass feedstock during hydrotreatment. As discussed, fast pyrolysis of lignocellulosic biomass is a relatively economical way to produce pyrolysis oil. As such, an efficient integrated hydrotreating definitely offers remarkable potential for production of renewable liquid bio-based diesel and gasoline from lignocellulosic biomass.

Over the past decades, several catalytic systems, namely hydrolysis, liquefaction, gasification, pyrolysis and deoxygenation/hydrogenation for the catalytic conversion of lignocellulosic biomass have increasingly received attention. Generally, acid catalysts are primarily used in the catalytic hydrolysis of lignocellulosic biomass to produce glucose and xylose; metal supported catalysts and zeolites are primarily evaluated in the gasification of lignocellulosic biomass to produce H2 or syngas; and alkaline catalysts are dominantly investigated in the fast pyrolysis. Over multifunctional catalysts, the integrated hydrotreatment of lignocellulosic biomass specifically lead to sorbitol and mannitol, EG or hydrocarbon-based diesel and gasoline.

Theoretically, the scale-up of a chemocatalytic process of lignocellulosic biomass can produce fuels and chemicals in large quantities in a short reaction period. However, no matter what type of catalytic processes employed, present techniques have not yet met the required level for commercialization in an economical and environmentally stable fashion. The present liquefaction, gasification and pyrolysis of lignocellulosic biomass yield very complicated products in most cases. The upgrading and separation of products requires high energy consumption. The invention of a heterogeneously solid catalyst with extraordinary activity and selectivity remains an essential task of paramount importance. A paradoxical, challenging issue is that the heterogeneous reaction over solid catalysts commonly suffers from low catalytic activity due to the solid–solid contact between the insoluble lignocellulosic biomass and solid catalyst. The utilization of ionic liquids as solvents and/or as catalysts provides an alternative solution. However, the use of the ionic liquids might bring about new problems such as separation and extraction of the targeted products and increased cost.

Fast pyrolysis of lignocellulosic biomass has proven to be more efficient than liquefaction and gasification. It is expected that upgraded pyrolysis oils can act as fuels directly. However, provided that gasification processes can selectively produce syngas with cost-effective cleaning technology, it is also certainly of great commercial value because syngas can be converted to clean fuels and fine chemicals by currently available catalytic technologies, for example syngas to methanol and ethanol and then to hydrocarbons and olefins.222 Also, it is much desired to directly gasify and pyrolyze wet lignocellulosic biomass because drying lignocellulosic biomass is an energy-intensive and time-consuming operation.224

In the short term, fossil crude oils are still available in large quantities. Therefore, the overall costs for production of commodity fuels and chemicals from lignocellulosic biomass processes by the present catalytic techniques are indeed less competitive in comparison with large-scales petroleum industries. In the long run, integrated production of fuels and fine commodity chemicals from lignocellulosic biomass feedstocks could be the most economical and renewable alternative in a sustainable society. To put the catalytic processes of lignocellulosic biomass into use, some key points to be addressed in the years ahead include:

1. In-depth understanding of the mechanism of the heterogeneously catalytic conversion of lignocellulosic biomass. It is necessary to identify the specific features of each component
such as cellulose, lignocelluloses and lignin in the reaction networks. It includes the interrelationship among the feedstock, the catalyst, the reaction conditions and the product distribution. In addition, the specific sources of lignocellulosic biomass to the desired products should also be established more clearly in each process.\textsuperscript{225} In-depth insights into the structure of cellulose and lignin biopolymers from the interdisciplinary sciences of plant and chemistry are surely useful to develop a strategy to convert it.\textsuperscript{226,227}

(2) Strategic design and preparation of multifunctional catalysts for highly active and selective conversion of lignocellulosic biomass. This involves acidity, basicity, metal-support interactions, the shape of catalyst particles, mechanical and chemical stability, deactivation and reusability. Because of the peculiar features of lignocellulosic biomass and its degraded products, novel reactors and separation systems, including process intensification, for continuous one-pass or one-pot operation should be developed so as to reduce the cost, minimize waste disposal and energy consumption, and maximize the productivity.

(3) Efficient production of liquid hydrocarbons from lignocellulosic biomass. Firstly, because liquid hydrocarbons can be directly used in current engines, there is no need for building new infrastructure for distribution. Secondly, if lignocellulosic biomass is to replace fossil oils mostly or even completely, similar to current petroleum industry, the large-scale process of lignocellulosic biomass should, for the most part, produce hydrocarbon-based liquid fuels. In addition to platform chemicals and fine chemicals, the identification of certain specific chemicals in the conversion of lignocellulosic biomass as a new type of fuels or fuel additives is also of much significance.\textsuperscript{228,229}

All in all, to make the catalytic conversion of lignocellulosic biomass into valuable products practicable is one of the most important topics in chemistry. It involves many challenges and opportunities. Though the studies on the chemocatalytic conversion of cellulose have received intensive attention over the past few decades and many breakthroughs have been achieved therein. A noteworthy thing is that besides cellulose, lignocellulosic biomass contains hemicellulose and lignin which are

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**Scheme 12**  (A) Reaction scheme and key performance factors for the individual process steps in the formation of valeric biofuels (S: selectivity, [mol%]; P: productivity, $[\text{productug}^{-1}\text{h}^{-1}]$; and C: concentration, [wt%]). LA: levulinic acid; gVL: g-valerolactone; VA: valeric acid; EV: ethyl valerate; EG: ethylene glycol; PG: propylene glycol; IER: acidic ion-exchange resin. (B) Probable reaction mechanism for the conversion of gVL to VA over bifunctional catalysts. MTHF: methyl tetrahydrofuran; Pe: 1-pentanol; PV: Pentyl valerate; PeOH: 1-pentanol.\textsuperscript{218} Adapted and reprinted with permission from ref. 218. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
still less investigated. Moreover, the most workable and economical way could be to use lignocellulosic biomass directly, rather than pure cellulose. It might be right to say that the technology of catalytic conversion of lignocellulosic biomass to fuels and chemicals remains in its infancy. Recent advances have shown an exciting prospect of putting catalytic conversion of lignocellulosic biomass to good use. The next decades will certainly witness the use and growth of catalytic production of fuels and chemicals from lignocellulosic biomass with continual technological innovations.

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