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## Targeted chemical upgrading of lignocellulosic biomass to platform molecules

J. S. Luterbacher,<sup>†a,b</sup> D. Martin Alonso<sup>a</sup> and J. A. Dumesic<sup>\*a,b</sup>

This review presents an overview of the initial targeted chemical processing stages for conversion of lignocellulosic biomass to platform molecules that serve as intermediates for the production of carbon-based fuels and chemicals. We identify four classes of platform molecules that can be obtained in an initial chemical processing step: (i) sugars, (ii) dehydration products, (iii) polyols and (iv) lignin monomers. Special emphasis is placed on reporting and comparing parameters that affect process economics and/or sustainability, including product yields, amount of catalyst used, processing conditions, and product concentrations. We discuss the economic trade-offs associated with choices related to these parameters, depending on the product that is targeted. We also address the effects of real biomass on the ability to recover, recycle, and potentially regenerate catalysts and solvents used in the biomass conversion processes.

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<sup>a</sup>Department of Chemical and Biological Engineering, Engineering Hall, University of Wisconsin-Madison, Madison, WI 53706, USA. E-mail: dumesic@engr.wisc.edu;

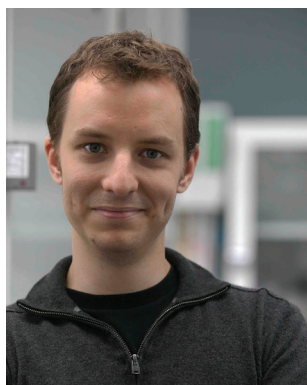
Fax: (+1) (608) 262-0832

<sup>b</sup>Great Lakes Bioenergy Research Center, 1552 University Ave, Madison, WI 53726, USA

<sup>†</sup>Present address: Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

### 1. Introduction and scope of review

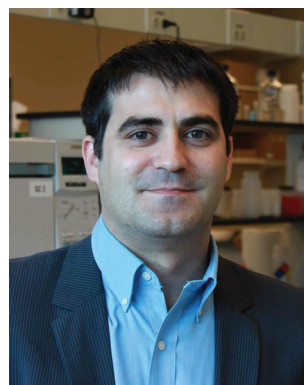
Most carbon-based products (*i.e.*, plastics, pharmaceuticals, cosmetics, pigments, *etc.*) that our society uses on a daily basis are derivatives of petroleum, and thus require the continued exploitation of fossil fuel resources. The global community, increasingly aware of resource depletion and climate-change dangers linked to fossil resource use, is thus seeking renew-



**J. S. Luterbacher**

Professor Jeremy S. Luterbacher earned his B.S. and M.S. in Chemical Engineering from the École Polytechnique Fédérale de Lausanne (EPFL), Switzerland, in 2005 and 2007. In 2006, he moved to MIT to work as a visiting M.S. student in Professor Jefferson Tester's research group. He obtained his PhD at Cornell University in 2012 under the supervision of Professors Larry P. Walker and Jefferson W. Tester, now at Cornell. He

then moved to UW-Madison to work as a postdoc with Professor James A. Dumesic. In 2014, he returned to EPFL as an Assistant Professor to continue research in the fields of biomass conversion, heterogeneous catalysis and biocatalysis.



**D. Martin Alonso**

Dr Martin Alonso earned his Bachelor degree in Chemical Engineering from the University of Salamanca (Spain) and his PhD from Catalysis and Petroleum-chemistry Research Institute (Spain) under the supervision of Dr Rafael Mariscal working in the production of biodiesel using heterogeneous catalysis. In 2009 he moved to UW-Madison to work with Prof. James A. Dumesic as a Research Associate at the University of Wisconsin-

Madison studying new catalytic processes to convert lignocellulosic biomass into valuable chemicals and fuels. He is (co)author of 9 patents and 40 peer-reviewed manuscripts and book chapters and currently he is part of a start-up company, Glucan Biorenewables LLC focused on the production of chemicals from biomass.

able alternatives.<sup>1</sup> Countries that have large biomass resources, such as the United States, have identified biofuels as a potential sustainable contributor of up to 30% of liquid fuels by 2030.<sup>2</sup> Furthermore, for certain products, biomass-derived alternatives appear to be the only renewable option. Direct biomass-derived alkanes are the main renewable substitutes that are being considered for specialty transportation fuels such as diesel or jet fuel, which cannot easily be replaced by electricity or ethanol.<sup>3–5</sup> When considering alternative carbon-based raw materials for the petrochemical industry, options are even more limited. There are only two large-scale sources of renewable carbon on this planet: plants and atmospheric carbon dioxide. Although options exist for converting atmospheric CO<sub>2</sub> to liquid products, they are currently more complicated and costly than those used for utilization of plant-based resources.<sup>6</sup>

The bulk of terrestrial biomass is represented by lignocellulosic biomass, which is mainly composed of structural polysaccharides. Approximately 30–50% is cellulose, a polymer of glucose; and 20–35% is hemicellulose, a hetero-polymer containing mostly xylose. Lignin comprises most of the remainder of biomass, and it is a complex heteropolymer containing aromatic alcohol units.<sup>2,7</sup> Successfully replacing petroleum based fuels and chemicals with lignocellulosic biomass-based products will require high-yield, low-cost and energetically efficient targeted upgrading processes. Because polysaccharides form the bulk of biomass weight, they have been the principal focus for targeted upgrading processes, especially considering the well-known chemistry and biochemistry for upgrading carbohydrates. Lignin upgrading has been

more challenging in view of its complexity and higher monomer and bond diversity.

Polysaccharides can be converted to useful products through several intermediates (Fig. 1). All targeted upgrading routes involve an initial depolymerization of the polysaccharides to produce soluble C<sub>5</sub> (from hemicellulose) or C<sub>6</sub> sugars (from cellulose). However, some processes directly produce dehydration products (furfural, 5-hydroxymethylfurfural or HMF, levulinic acid and formic acid) or sugar alcohols (sorbitol, xylitol, *etc.*) in a single stage upon formation of the sugar. Lignin often partially depolymerizes under the same conditions required to depolymerize polysaccharides, but it requires additional chemical processes (subsequent or simultaneous) such as hydrogenolysis or oxidation to yield monomers (Fig. 1). These initial processes are necessary to provide small molecules, which can then be converted to other molecules, often with lower functionality and reduced oxygen content. This approach differs from the transformation of petroleum molecules, which typically involves adding functionality and sometimes increasing oxygen content.<sup>8</sup>

All of the routes depicted in Fig. 1 can be active during the initial processing of lignocellulosic biomass, and the products formed from these routes thus serve as platform molecules for the targeted upgrading of biomass to fuels and chemicals. By focusing on these defined chemical upgrading pathways or “targeted upgrading” approaches illustrated in Fig. 1, we exclude several important chemical upgrading routes such as gasification, pyrolysis or hydrothermal liquefaction from the scope of this review. Since these routes are thermally driven processes that generally involve multiple simultaneous and subsequent reactions, we consider them to be outside of what we refer to as “targeted chemical upgrading”. However, several other recent reviews have covered these subjects in detail.<sup>9–17</sup> Another widely studied route for initial biomass processing is pretreatment and enzymatic hydrolysis. In this process, an initial thermochemical or pretreatment stage partially extracts some of the hemicellulose and lignin fraction of biomass to increase accessibility to the cellulose and remaining hemicellulose for enzymes added in a subsequent hydrolysis stage. Many recent reviews have covered pretreatment and enzymatic processes.<sup>18–28</sup> Thus, we have chosen to focus this review on those processes that exclusively involve the thermochemical conversion of biomass, and exclude processes, such as pretreatment, that must systematically be coupled with enzymatic hydrolysis. Furthermore, a debate has recently arisen concerning the possible cost of enzymes in an industrial biorefinery, with certain studies arguing that these costs have been underestimated.<sup>29</sup>

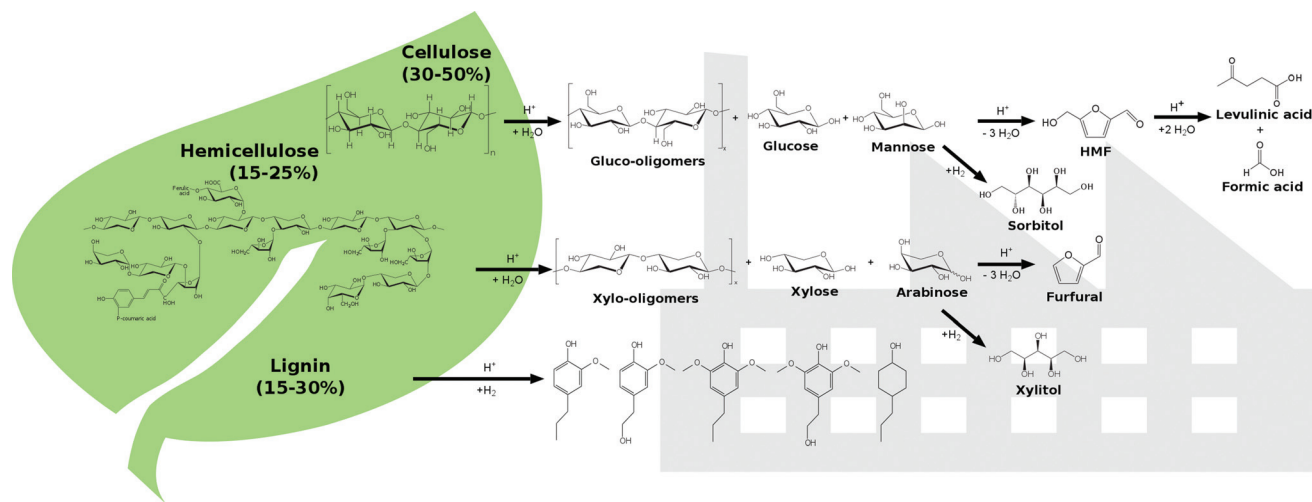
Many studies have investigated the processing of biomass-derived model compounds, including pure cellulose, glucose, xylose, furfural, *etc.* However, this review will focus exclusively on the processing of real lignocellulosic substrates to represent the initial processing in a biorefinery. Moreover, this review will address the main parameters that affect the cost and environmental impact of the process, namely the amount of



**J. A. Dumesic**

*Professor James A. Dumesic earned his B.S. degree from UW-Madison and his M.S. and Ph.D. degrees from Stanford University, under the supervision of Professor Michel Boudart. Dumesic joined the Department of Chemical Engineering in 1976, and he is currently the Steenbock Chair in the College of Engineering and the Michel Boudart Professor of Chemical and Biological Engineering. Throughout his career, Dumesic*

*has used spectroscopic, microcalorimetric, and reaction kinetics techniques to study the surface and dynamic properties of heterogeneous catalysts. Dumesic elucidated aqueous-phase reforming as a catalytic process to produce H<sub>2</sub> and/or value-added chemicals from biomass-derived sugars and polyols; he developed new approaches for the production of gamma-valerolactone (GVL) from the cellulose and hemicellulose fractions of lignocellulosic biomass; and he is currently studying the use of GVL as a solvent for biomass processing.*



**Fig. 1** Targeted chemical upgrading of lignocellulosic biomass. The products depicted above have all been produced in a single catalytic process from lignocellulosic biomass. Only sugars that can account for over 5 wt% of lignocellulosic biomass are included and only those molecules that have reportedly been produced in yields above 10% are shown for lignin upgrading.

catalyst used, the processing conditions, the yields obtained, and the product concentrations achieved.

We will begin by discussing the principal processing strategies for depolymerizing biomass to produce sugars. We will then discuss the direct production of dehydration products furfural, levulinic acid and HMF. We will also discuss processes that have been the focus of fewer studies, such as the direct processing of real biomass to sugar alcohols or lignin monomers. Finally, we will provide a discussion of various processing strategies, and how these strategies are influenced by the economics of the catalyst and feedstock requirements.

## 2. Catalytic depolymerization of biomass to sugars

### Concentrated acid

The first efforts to depolymerize biomass structural polysaccharides were accomplished using concentrated sulfuric acid. As early as 1819, Braconnot observed that linen dissolved in concentrated sulfuric acid and, after being diluted and heated, produced an aqueous solution of glucose that could be fermented.<sup>30,31</sup> In the middle of the 20th century, industrial interest in biomass depolymerization grew significantly, and it was determined that acid recovery was a key factor for successful industrial implementation. Accordingly, several processes used HCl as the concentrated mineral acid, because it could be recovered by evaporation. A notable example was the Bergius–Rheinau process, which contacted wood with 42 wt% HCl for several hours and then used vacuum distillation at 309 K to recover about 80% of the HCl.<sup>32</sup> Between 60 and 66 wt % of the original wood could be recovered as soluble carbohydrates, corresponding to a carbohydrate yield of 90–95%.<sup>32</sup> After removal of the acid, a product containing precipitated

water-soluble carbohydrates of up to 90% sugars could be obtained. Despite impressive sugar recoveries and the high yields that could be achieved, the cost of HCl recovery as well and the amount of unrecovered HCl ultimately made the process uneconomical. More recently, a process developed by the company Viridia™ has built on the Bergius–Rheinau process using similar acid hydrolysis conditions and has obtained similar yields and product concentrations (Table 1).<sup>33</sup> The Viridia process uses solvent extraction to recover HCl, allowing them to reduce HCl loss and recovery costs. Some of the first patents filed by the company mention the use of an organic phase (such as mineral oil or other hydrocarbons) containing a water-insoluble organic acid and/or a water-insoluble amine.<sup>34–36</sup> This phase is used to extract HCl from the aqueous phase at room temperature. HCl can then be recovered by bubbling superheated steam through the organic phase at high temperature (420–490 K). Patents disclose that successful extraction solvents include hexanol, xylene, ethyl hexanol and mixtures of ethyl–hexanol and methanol.<sup>37,38</sup> A pilot plant of this process is currently in operation in Danville, Va.<sup>33</sup>

In the 1980s, Hoechst developed a similar process using gaseous HF with sugar yields of up to 85% glucose and 70% xylose.<sup>39</sup> The principal advantage of using HF was its low boiling point, which facilitates recovery. A separate study by Selke and Hawley demonstrated that a 99% yield of water-soluble carbohydrates could be recovered from wood using 10 ml of liquid HF and 1 ml of water for 1 g of wood<sup>40</sup> (Table 1). After evacuation of HF at 370 K for 5 h, less than 4 mg HF g<sup>-1</sup> wood remained.

All of the processes discussed above produce concentrated solutions of water-soluble carbohydrates. However, in all cases, a large fraction of these carbohydrates are in the form of oligomers, which may not be suitable for biological upgrading by

**Table 1** Conversion of untreated lignocellulosic biomass to soluble carbohydrates. Backslashes delimit conditions at separate processing stages

Feedstock	T (K)	Solvent	Time	Catalyst (concentration (wt%))	Product concentration (wt%)	Soluble carbohydrate yield (%)		Source
						C <sub>5</sub>	C <sub>6</sub>	
<i>Concentrated acid</i>								
Wood	298–309	40% HCl in water	A few hours	HCl (40%)	90%	90–95% <sup>a</sup>		32
Wood	298/394	66% HCl in water	1 h/1 h	HCl (66%)	14%	95%	80%	206
Wood	283–288	42% HCl in water	5–15 h	HCl (42%)	77%	95%		37,183,207
Wood	363	Gaseous HF	N.R.	23 wt% HF	77%	70–85%		39
Wood	296	90% HF in water	1 h	90% HF	50–100%	99%		40
Corn cobs	293	70 : 30 H <sub>3</sub> PO <sub>4</sub> –H <sub>2</sub> SO <sub>4</sub>	3 h	70 : 30 H <sub>3</sub> PO <sub>4</sub> –H <sub>2</sub> SO <sub>4</sub>	11%	90%	80%	42
<i>Mechanocatalytic</i>								
Beechwood	315	None	2 h	8% H <sub>2</sub> SO <sub>4</sub>	90%	100%		43
Beechwood	315/410	None	2 h/1 h	8% H <sub>2</sub> SO <sub>4</sub>	10%	92%	93%	46
Corn stover	298	None	2 h	50% Kaolinite	100%	60%		44
Aspen wood	298	None	2 h	50% Kaolinite	100%	40%		44
<i>Dilute acid</i>								
Douglas fir	440/500	Water	11 min/35–40 s	1.1/0.8 wt% H <sub>2</sub> SO <sub>4</sub>	9–11%	87%	50%	52
Wood	458–466	Water <sup>b</sup>	about 3 h	0.53% H <sub>2</sub> SO <sub>4</sub>	3.6% (4.2%) <sup>c</sup>	68%		55
Wood	448–508	Water <sup>b</sup>	N.R.	0.8% H <sub>2</sub> SO <sub>4</sub>	3.6 wt%	95%	83%	53
<i>Hydrothermal</i>								
Wood	520/640	Water	20 s/1 s	—	2 wt% <sup>a</sup>	85%	60–64%	65,66
<i>Solvent-based approach</i>								
Corn stover	390/490	80 : 20 GVL–water <sup>a</sup>	60 min/30 min	1.5/0.05 wt% H <sub>2</sub> SO <sub>4</sub>	13 wt% <sup>d</sup>	70%	70%	78
<i>Ionic liquids</i>								
Corn Stover	378	[EMIM]Cl water	2.5 h/3.5 h	20 wt% HCl	0.9 wt%	79%	70%	83
Corn Stover	378	[EMIM]Cl water	3.5 h/3 h	10 wt% HCl	1.7 wt%	75%	66%	83
Switchgrass	433	[BMIM]Cl water	1.5 h	10 wt% HCl	2.6 wt% <sup>d</sup>	70%	82%	89

<sup>a</sup> Calculated using a generic biomass of the solvent is derived in flow-through mode. <sup>b</sup> Part is obtained after flashing. <sup>c</sup> Concentration of 40 wt% glucan and 20 wt% xylan. <sup>d</sup> After solvent extraction.

microorganisms. To produce monomers, the resulting products require a post hydrolysis step, usually consisting of diluting the oligomers with water and hydrolyzing them in a dilute acid environment (0.5–5 wt% acid). In the case of processes involving HCl, sufficient acid remains to hydrolyze the resulting oligomers to monomers. In the case of HF use, recovery of the mineral acid was so efficient that additional acid had to be added for the post-hydrolysis process. Quasi-quantitative conversion of oligomers to monomers was achieved in after 1 h at 410 K in the presence of 50 mM H<sub>2</sub>SO<sub>4</sub>.<sup>40</sup>

The high sugar yields achievable with concentrated acid have made this the standard method for analyzing biomass structural polysaccharides. This method consists of treating a sample in 72 wt% sulfuric acid at room temperature for 1 h to recover all polysaccharides as soluble sugars.<sup>41</sup> The solution is then diluted with water to reach 4% H<sub>2</sub>SO<sub>4</sub>, and it is heated to 374 K for 1 h to further hydrolyze any oligomers to monomers. This second step is sometimes referred to as the post-hydrolysis step, and includes the use of pure sugar standards treated at identical conditions to determine the extent of degradation (usually less than 5%). Recently, it was shown that using 7 : 3 mixtures of phosphoric and sulfuric acid significantly increased the stability of hemicellulose sugars in acid even at

long reaction times. This method achieved high soluble carbohydrate yields (80–90%) with a high-solids reaction (20 wt% solids).<sup>24</sup> This approach allowed monomers to be produced with minimal degradation and without any dilution simply by heating the solution to 358 K for 4 h. However, the high boiling points of sulfuric (610 K) and phosphoric acid (431 K) eliminate the possibility of recovering these mineral acids by evaporation.

In summary, all of the concentrated acid processes can generally achieve high yields at high product concentrations (Table 1), but they suffer from the need to recover a large fraction of the mineral acid to be economical.

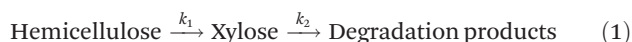
### Mechanocatalytic processes

By combining mechanical milling with the use of a catalyst, lignocellulosic biomass can be depolymerized using lower amounts of mineral acid<sup>43</sup> and/or solid acid catalysts.<sup>44,45</sup> Close to 100% solubilization of biomass carbohydrates was achieved for beechwood and sugarcane bagasse, with only 8 wt% H<sub>2</sub>SO<sub>4</sub> in a solvent-free system after 2 h of ball milling (Table 1). Similar results were obtained with about 2 wt% HCl, the volatility of which could enable at least partial recovery of the acid.<sup>43</sup> This also allowed for an easier impregnation of the

biomass using gaseous HCl. When using H<sub>2</sub>SO<sub>4</sub>, the authors reported the need to use an organic solvent, such as diethyl ether, that is then evaporated to ensure homogeneous impregnation. In a more recent study, the same authors demonstrated that the sugars solubilized with sulfuric acid could be converted to monomers at around 90% yield once diluted in water and hydrolyzed at 410 K for 1 h, resulting in a 10 wt% solution.<sup>46</sup> When 50 wt% of modified Kaolinite was used as a solid acid catalyst, soluble sugar yields ranging between 50% (Aspen wood) and 60% (corn stover) were obtained with this more easily recoverable acid catalyst. Therefore, mechanocatalytic processes can achieve similar results to concentrated acid processes using lower amounts of acid, thereby reducing acid recovery costs (Table 1). However, a key parameter in determining the scalability of these processes is the electrical energy requirements of the mechanical milling, which are projected to be significant. Estimates of this electrical energy requirement vary between 11 and 100% of the energy of ethanol that could be produced from the resulting sugars, depending on assumptions regarding yields and milling conditions.<sup>43,44</sup>

### Dilute acid

Biomass can be hydrolyzed to sugars using dilute acid solutions (<5 wt% acid). However, this approach requires significantly higher temperatures (440–570 K),<sup>47</sup> at which both glucose and xylose undergo dehydration to furans and re-polymerization to form humins, a solid by-product formed from sugars and/or furans.<sup>48</sup> This issue has been represented for both hemicellulose<sup>49</sup> and cellulose<sup>50,51</sup> by modeling two sequential reactions:



In each of these models, the acid concentration influenced the kinetic constants according to the following relation:

$$k_i = [\text{Acid}]^n k_{0,i} \exp\left(\frac{E_{a,i}}{RT}\right) \quad (3)$$

Because these models describe experimental results, they can be used to determine maximum carbohydrate yields obtainable at given acid concentrations. For example, in about 1 wt% H<sub>2</sub>SO<sub>4</sub>, a xylose yield of close to 90% from xylan can be obtained after a few minutes at 450 K, and a glucose yield of close to 60% from cellulose can be obtained after about 10 s at 510 K (Fig. 2).

These results suggest that a dual stage hydrolysis process could be developed to produce soluble carbohydrates from lignocellulosic biomass (see a depiction of this process in Fig. 3). Such a process was developed and run at pre-pilot plant scales (two batch reactors, with a capacity of 100 kg per run of initial biomass) in the 1980s at the Forest Products Laboratory in Madison, WI.<sup>52</sup> In this process, a first hydrolysis stage was employed at 440 K for 11 min in the presence of a 1.1 wt% H<sub>2</sub>SO<sub>4</sub> solution. The resulting slurry was washed to produce an initial hydrolysate solution containing 10 wt% sugars, representing 88% yield of the original xylose (Table 1). The remaining cellulose-rich solids were treated in a subsequent hydrolysis stage at 500 K for 35–40 s in the presence of a solution containing 0.8 wt% H<sub>2</sub>SO<sub>4</sub> (Table 1). The slurry remaining in the reactor was washed to produce a solution containing 11 wt% carbohydrates and a 42% yield of glucose. However, accounting for the glucose that was removed during the first hydrolysis stage, the overall glucose yield from glucan reached 50%. This low glucose recovery demonstrates the difficulty of achieving high glucose yields in a batch or tubular process, due to high rates of glucose degradation compared to

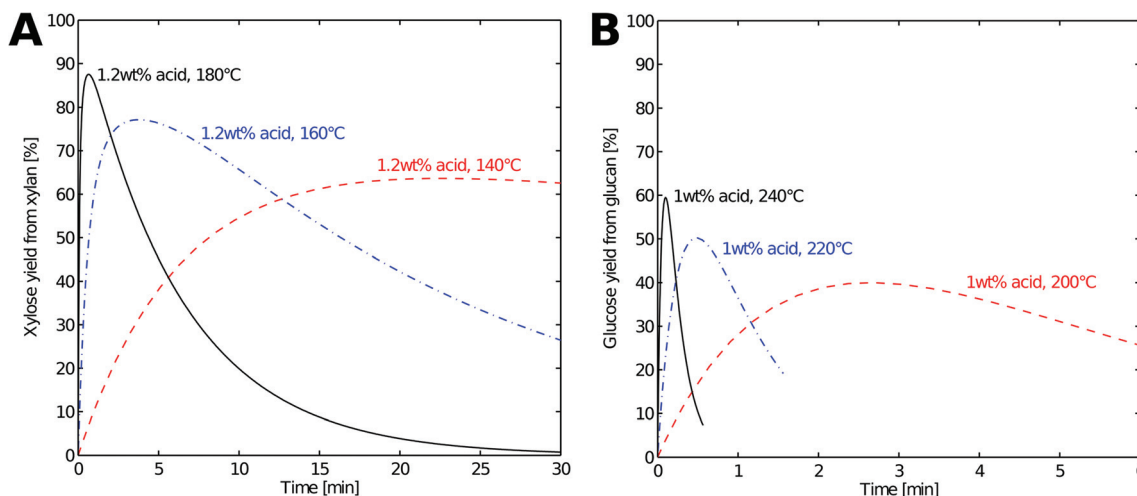


Fig. 2 Xylose (A) and glucose (B) yields obtained with dilute acid hydrolysis of hardwood. Xylose (A) yields were obtained using kinetic parameters reported by Esteghlalian *et al.*<sup>49</sup> for poplar and glucose (B) yields were obtained using kinetic parameters obtained by Fagan *et al.*<sup>50</sup> for newsprint waste.

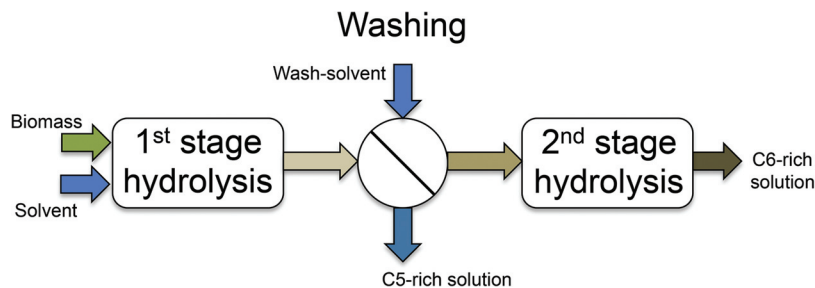


Fig. 3 Two-stage chemical hydrolysis system. Hemicellulose sugars are extracted during a first stage at a low temperature (430–510 K depending on acid concentration and residence time) and cellulose sugars are extracted during a second stage at a higher temperature (500–670 K depending on acid concentration and residence time).

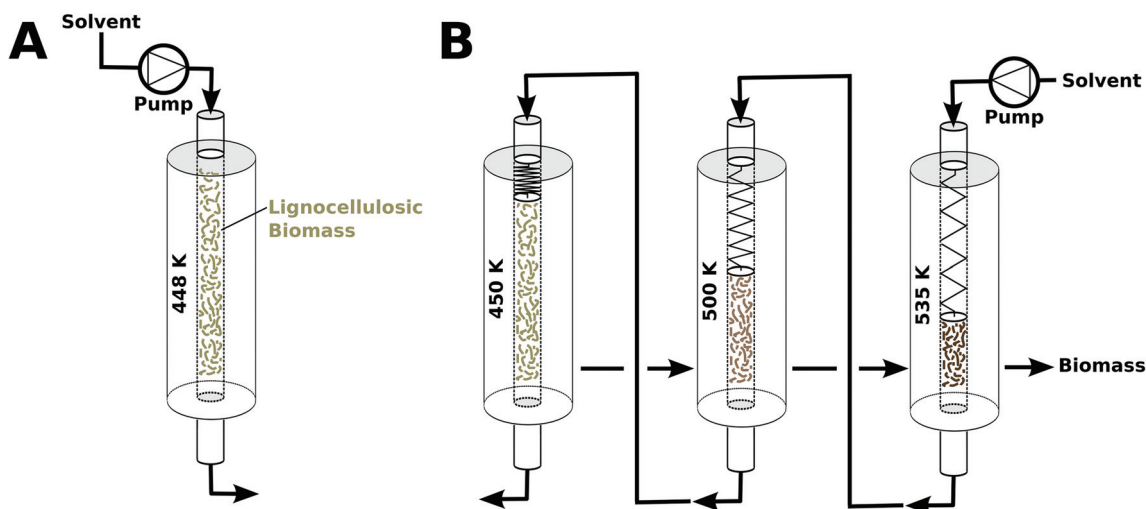


Fig. 4 Flow-through reaction systems for lignocellulosic biomass hydrolysis. (A) Single flow-through reaction system. (B) Three stage counter-current flow-through reaction system.

those of cellulose depolymerization. High yields are achievable by increasing temperatures and shortening residence times (Fig. 2B). However, this combination leads to increasingly difficult processing conditions.

A semi-batch or flow-through reaction system can be used to decouple the residence times of the solid carbohydrate from its soluble counterpart. In such a system, an aqueous dilute acid solution is flowed through a heated packed bed of biomass (Fig. 4A). According to reaction kinetics studies, flow-through systems are typically limited by their ability to produce concentrated soluble carbohydrate solutions and high sugar yields simultaneously. Typically, 45 to 55% glucose yields are predicted for the production of a 2 to 4 wt% sugar solution using 1 wt%  $\text{H}_2\text{SO}_4$  in water.<sup>53</sup> This system was first developed as part of the Scholler process in Germany during the 1920s.<sup>54</sup> It was then optimized at the Forest Products Laboratory in Madison, WI.<sup>55,56</sup> In the latter process, a typical mass balance in a pilot plant built in collaboration with the Tennessee Valley Authority demonstrated total carbohydrate yields close to 70% while producing a sugar solution of 3.6 wt% (4.2 wt% after flashing to room temperature)<sup>56</sup> (Table 1).

Only total reducing sugars were reported, but this would correspond to a glucose yield of about 55% if 95% xylose was recovered.

Studies carried out at the National Renewable Energy Laboratory (NREL) have reported three strategies that can be used to increase sugar yield and concentration in biomass flow-through reaction systems:<sup>53,57</sup>

- Multiple hydrolysis temperature stages: running the flow-through reaction setup at a single temperature can lead to increased degradation of hemicellulose sugars due to the higher temperature required to hydrolyze cellulose. Therefore, running the reaction at two or more sequentially increasing temperatures enables the use of temperatures optimally suited for both cellulose and hemicellulose reactions.

- Counter-current operation: modeling of reaction kinetics has demonstrated that, in the case of continuous operation, counter-current flow, where fresh biomass is fed into the bottom of a reactor and a higher rate of solvent is flowed-through from the top, produces better results than co-current flow-through or batch flow-through.<sup>58</sup> This behavior can be understood by realizing that the highest rate of sugar pro-

duction occurs in the presence of the least treated biomass, which contains the most polysaccharides. Therefore, to minimize degradation, fresh biomass should enter the reactor at the closest point to the solvent outlet. The entry of fresh biomass coincides with the solvent outlet in the case of continuous counter-current flow-through operation.

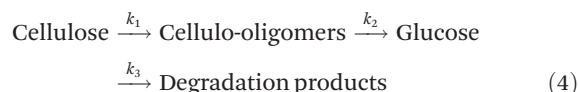
• Shrinking bed operation: As the reaction progresses and the bed loses mass, compression of the packed bed avoids void volume formation and decreases the residence time of any soluble molecules detaching from the bed, which reduces time for degradation.

Researchers at NREL built a three-stage reactor at three distinct temperatures that attempted to mimic the behavior of a continuous counter-current reactor with a shrinking bed, thus implementing these three strategies (Fig. 4B). Using this reaction system, they report increased yields of 95% for xylose and 80% for glucose, while still producing a solution containing 3.6 wt% sugars (Table 1).

### Hydrothermal processes

To achieve yields above 60% with 1% H<sub>2</sub>SO<sub>4</sub>, high temperatures (>500 K) and short residence time (<1 min) are required<sup>50,51</sup> (Fig. 2A). The same trend is observed when pure water is used as the hydrolysis medium for cellulose. In such a system, the equilibrium concentration of protons in water is sufficient to catalyze cellulose hydrolysis, especially at higher temperatures, where this concentration increases as the pK<sub>w</sub> of water decreases from 14 to 11.2 between 298 and 523 K.<sup>59</sup> However, for a wide range of temperatures, carbohydrate degradation is faster than cellulose or hemicellulose depolymerization, leading to low product recovery (*i.e.*, below 30% at 550 K<sup>60</sup>). As demonstrated by recently reviewed reaction kinetics data,<sup>16</sup> cellulose depolymerization becomes faster than glucose degradation starting around 620 K (Fig. 5A) due to its higher activation energy. Therefore, processes at high temperature with short residence times may yield interesting results.

The same kinetic model that was used in acid hydrolysis (eqn (2)) can be used for pure water systems with the temperature-dependent kinetic constants predicted by the two Arrhenius regressions shown in Fig. 5A. Using these data, yields of 40% and 80% are predicted for a reaction run at 620 K for 1 s and 720 K for 10 ms, respectively (Fig. 5B). However this kinetic model does not account for oligomers, which in pure water, can contribute significantly to the yield of soluble sugars. To account for cellulose oligomers, the following relationship can be used:



Values for kinetic constants  $k_1$  and  $k_3$  can be taken from the two Arrhenius regressions shown in Fig. 5A. Zhao *et al.* proposed a kinetic model for cellulo-oligomer hydrolysis to monomers that can be used as a first approximation to provide yields with soluble *gluco*-oligomers, which could reach over 90% after 10 ms at 720 K (Fig. 5B, insert). In practice, these conditions are difficult to attain and any results are likely to be dependent on the specific reaction system due to heat transfer and mass transfer limitations. Nevertheless, several groups have obtained results that are consistent with kinetic predictions. Sasaki *et al.* obtained total sugar yields between 65% and 77% after 10–50 ms at 675 K,<sup>61</sup> and Cantero *et al.* reported yields over 95% for residence times between 10 and 30 ms at the same temperature (although they indicate that their oligomer measurements are estimates based on aggregated HPLC areas, rather than on glucose measurements done after post hydrolysis acid treatment).<sup>62,63</sup>

Despite the difficulty of developing an industrial process based on these high temperatures and short residence times, the company Renmatix® has developed extensive intellectual property in this area and describes its Plantrose™ process as relying on a two-stage process similar in concept to the one

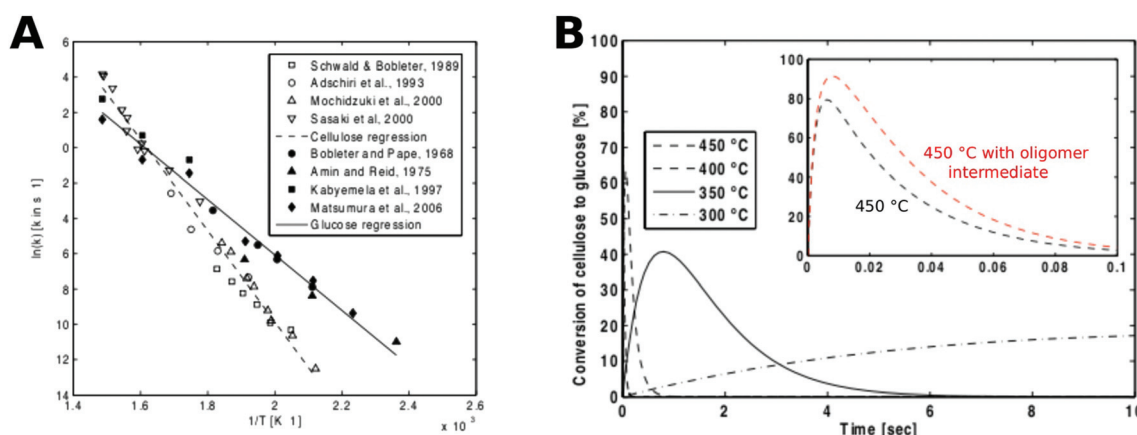


Fig. 5 (A) Comparison of Arrhenius plots for cellulose and glucose degradation (adapted from Peterson *et al.*<sup>16</sup>). Kinetic data was taken from Schwald and Bobleter,<sup>199</sup> Adschiri *et al.*<sup>200</sup> Mochidzuki *et al.*<sup>201</sup> Sasaki *et al.*<sup>61</sup> Bobleter and Pape,<sup>202</sup> Amin and Reid,<sup>203</sup> Kabyemela *et al.*<sup>204</sup> and Matsumura *et al.*<sup>205</sup> (B) Predicted glucose production from cellulose in pure water. Insert is a close-up for short reaction times. The red curve represents glucose and oligomer production when oligomers are included.

presented for dilute acid (Fig. 3).<sup>64</sup> In the first processing stage, lignocellulosic biomass in water is subjected to temperatures of about 520 K for 20 s to hydrolyze the hemicellulose portion of the biomass.<sup>65,66</sup> Although they are using higher temperatures and shorter residence times, this process is similar to the xylan removal that occurs during biomass pretreatment processes using hot water (sometimes referred to as auto-hydrolysis processes).<sup>67–70</sup> In the second stage, the remaining solids are washed to remove soluble hemicellulose sugars and then heated to 640 K for 1–2 s to hydrolyze the remaining cellulose.<sup>65,66</sup> In their patent application, Renmatix report a xylose yield of 85% during first stage and a glucose yield up to 64% during the second stage, a yield similar to that obtained by Sasaki *et al.* for pure cellulose.<sup>61,65</sup> However, it is unknown if these results can be replicated at industrially relevant concentrations. The patents filed by Renmatix® report using slurries of 4 wt% solids during the first and second hydrolysis stage.<sup>65,66</sup> Assuming hemicellulose and cellulose contents of about 20 and 40 wt%, respectively, this loading would correspond to soluble carbohydrate concentrations of about 2 wt% (Table 1). In another patent, a 20 wt% solids process is mentioned for the first hydrolysis stage (hemicellulose removal), although no specific solid content is mentioned for the second hydrolysis stage and no sugar yields are mentioned for either stage.<sup>71</sup> Since heat and mass transfer issues increase with increasing solid content, obtaining these yields at higher solid contents using such short residence time processes could be difficult.

Patents filed by Renmatix® also mention the use of several organic or inorganic acids that could be used to acidify the medium including sulfuric, hydrochloric, phosphoric and oxalic acid.<sup>66,72</sup> They also mention using CO<sub>2</sub>, either subcritical or supercritical, to acidify their medium through the formation of carbonic acid.<sup>65</sup> This approach is similar to that proposed by several groups who used supercritical CO<sub>2</sub> in combination with water during pretreatment and observed improved yields.<sup>73–77</sup> In one of the Renmatix® process embodiments where 0.2% H<sub>2</sub>SO<sub>4</sub> is used, approximately 90% yield of cellulose-soluble sugars is reported after 1 s at 510 K.<sup>65</sup> These conditions are similar to those reported by the two-stage process described by the Forest Products Laboratory (500 K, 35 s, 0.8 wt% H<sub>2</sub>SO<sub>4</sub>) but with higher yields (88% *vs.* 50%).<sup>52</sup> The difference in yield could in part be due to the difference in solid content at the start of hydrolysis (4 wt% *vs.* 24% solids), which can significantly hinder yields.

### Solvent-based approaches

Recently, we have shown that  $\gamma$ -valerolactone (GVL), a polar aprotic molecule that can be produced from biomass, could be used as a co-solvent with water for the complete saccharification of biomass using low acid concentrations (1.5–0.05 wt% H<sub>2</sub>SO<sub>4</sub>).<sup>78</sup> Using a flow-through reaction setup (Fig. 4A), and a temperature ramp between 430 and 490 K, soluble carbohydrate yields between 70% and 90% were obtained. Due to the previously observed increased formation of dehydration products from sugars in GVL compared with undesirable

re-polymerization by-products such as humins,<sup>79</sup> total yields to detectable products increased to 85–95% when furfural, HMF or levulinic acid were included. Using the same flow-rate and decreasing the temperature ramp time from 120 to 30 min, increased concentrations to about 1.5 wt% sugars from 0.5 wt%, while maintaining yields of 70% for C<sub>6</sub> sugars and 80% for C<sub>5</sub> sugars. These high yields are due to the GVL's ability to selectively lower the apparent activation energy of polysaccharide hydrolysis compared to that of the competing sugar dehydration reactions to furans, which lower carbohydrate yields.<sup>80,81</sup> We have proposed that, based on kinetic evidence, the acid-catalyzed rate increases seen in GVL, and similar polar aprotic solvents such as THF, are due to the changing stabilization of the acidic proton relative to the transition state when the solvent is present.<sup>80</sup> Furthermore, the addition of liquid CO<sub>2</sub> to the GVL-water-sugar mixture led to the formation of a gas-expanded GVL phase that spontaneously separated from the aqueous phase and that retained up to 90% of the sugars. After 3 extractions, over 99.5% of the GVL could be removed from the aqueous phase while leaving 80% of the original sugars to form a 7.2 wt% aqueous sugar solution. Concentrations could be further increased by treating a 20 wt% slurry of original biomass in a batch process at 390 K for 1 h in the presence of the same GVL solvent and 1.5 wt% H<sub>2</sub>SO<sub>4</sub>. This stage densified the biomass by removing some of the C<sub>5</sub> sugars and the lignin, which allowed for increased biomass loading in the flow-through reactor. Overall, C<sub>5</sub> and C<sub>6</sub> sugar yields were maintained at about 70%. After 3 extractions with CO<sub>2</sub>, an aqueous solution that contained 90% of the solubilized sugars and less than 0.5 wt% of the original GVL and had a sugar concentration of 12.7 wt% was obtained.

### Ionic liquids

Ionic liquids can be used to completely solubilize cellulose, which can then be hydrolyzed in dilute acid conditions.<sup>82,83</sup> However, soluble sugars are particularly prone to dehydration in the presence of ionic liquids and mineral acids, leading to moderate yields.<sup>83–86</sup> The use of solid acid catalysts led to similarly low yields.<sup>87</sup> For this reason, ionic liquids had initially been proposed as interesting solvents for the production of HMF from cellulose.<sup>88</sup> Carbohydrate stability is significantly improved in the presence of water, but water causes the precipitation of cellulose and low yields of glucose.<sup>83</sup> However, Binder and Raines have demonstrated that progressive addition of water as hydrolysis takes place increases overall glucose stability while preventing early precipitation of cellulose. Glucose yields of 89% after 4 hours of reaction at 378 K were achieved using a 1 wt% HCl solution in 1-ethyl-3-methylimidazolium chloride and progressively increasing the water level from 5 to 43 wt% over the course of one hour.<sup>83</sup> With corn stover, significant amounts of unconverted polysaccharides (mostly cellulose) precipitated during the progressive addition of water leading to low glucose yields. However, by repeating their process with the unconverted solids, additional glucose and xylose could be recovered, and overall yields of 70% and 79% could be reached for glucose and xylose, respect-



ively (Table 1). However, these yields were obtained at low concentrations of about 1.7 wt% sugars (before dilution) and required separation of the aqueous sugar stream and ionic liquids by chromatography.

Using a similar protocol with switchgrass and 1-*n*-butyl-3-methylimidazolium chloride, Sun *et al.* obtained yields of 82% and 69% for glucose and xylose, respectively.<sup>89</sup> They demonstrated that adding a concentrated NaOH solution produced a 15 wt% NaOH aqueous solution that spontaneously separated from the ionic liquid phase and that contained most of the sugars and only 0.4% of the ionic liquids. In addition, this separation step concentrated the sugars to a level of 2.6 wt% (Table 1). However, significant loss of sugars occurred during alkali extraction, presumably due to degradation, lowering the yields to about 50% for both glucose and xylose.

### 3. Furans and their derivatives

#### Furfural

Furfural is one of the few chemicals that is produced commercially from lignocellulosic biomass. It is obtained by the acid dehydration of pentoses (such as xylan). Current production is based on the Quaker Oats process,<sup>90</sup> in which biomass is mixed with sulfuric acid and introduced in a cylindrical horizontal cooker, which rotates and serves as a reactor. The reaction begins when pressurized steam is fed into the reactor. This steam serves both for heating and as a stripping gas to remove the furfural as it is produced. Removing the furfural is necessary to prevent further degradation, as furfural can polymerize (resinification), decompose, and react with the xylose (condensation). Once the furfural is in the vapor phase (1–6 wt% in water), it is purified, typically by distillation.

Over the years, the process for furfural production has been optimized with attempts to decrease the energy requirements; reduce the reaction time using higher temperature and acid concentration; make the process continuous using a tubular reactor (Supratherm process);<sup>91</sup> or to maximize the furfural yields by using a boiling reaction medium that minimizes furfural degradation by continuously removing it from the reaction medium (Suprayield process).<sup>92</sup> Several other processes have also been proposed in the last three decades, but the costs for furfural production have remained unchanged.<sup>93–96</sup>

A limitation of current methods for furfural production is that they typically lead to complete destruction of the C<sub>6</sub> fraction of biomass, which is typically treated as waste. Therefore, research has recently focused on co-producing furfural and other C<sub>6</sub> derived chemicals. Accordingly, researchers have tried to improve the yields of furfural from C<sub>5</sub> sugars and real lignocellulosic biomass by studying reaction mechanisms for furfural production and degradation reactions, and by using solid catalysts. Most of this work has been carried out using pure xylose or soluble C<sub>5</sub> sugars produced from biomass as feedstock. These studies have been extensively discussed and are outside the scope of this review.<sup>97–101</sup> We focus here on processes using lignocellulosic biomass.

One difficulty that arises in dealing with lignocellulosic biomass is the quantification of furfural yields. It is generally accepted that the calculations are based on biomass pentose content. However, it has been reported that in some catalytic systems, the hexose sugars can be converted to pentose sugars through a retro-aldol reaction<sup>102</sup> and be dehydrated to furfural. While this reaction is normally negligible, recently, yields up to 30% furfural from glucose have been reported.<sup>103</sup> A second problem is the correct analysis of the pentose content. Typically, xylose and arabinose are considered to be the source of furfural. However, it is possible that other compounds such as oligosaccharides containing uronic acid and xylose units,<sup>104</sup> which are not usually identified using traditional methods of xylan quantification by HPLC, can become potential sources of furfural. On other occasions, only xylan is considered as a source of furfural, because arabinose is less selective and is present in low amounts in lignocellulosic biomass.<sup>105,106</sup> These errors can lead to reports of higher molar yields of furfural when using lignocellulosic biomass compared to pure xylose.<sup>107</sup>

Research has focused on improving furfural production by two methods: (i) replacing the homogeneous catalyst by solid catalysts, and (ii) improving yields with reactions systems involving biphasic systems and organic solvents. Biphasic systems are often used in the production of furans from biomass, because they allow for the continuous extraction of the unstable furanic compound into the organic phase, thereby protecting it from the acid in the aqueous phase<sup>108,109</sup> (Fig. 6).

Gallo *et al.*<sup>105</sup> explored the utilization of zeolites with Brønsted and Lewis sites as active centers in a monophasic system. The Lewis acid catalyzes the isomerization of xylose to xylulose, and the Brønsted acid catalyzes the dehydration of xylulose to produce furfural.<sup>110–112</sup> In addition, the system showed to be particularly promising for conversion of arabi-

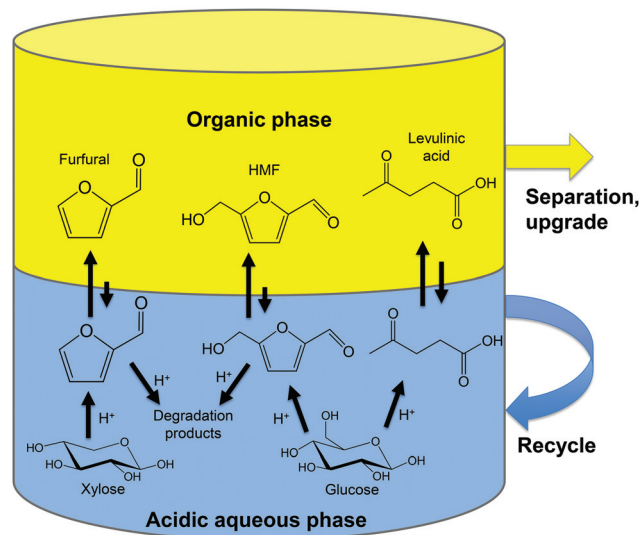


Fig. 6 Biphasic systems used for producing dehydration products from lignocellulosic biomass.

nose. In particular, the Lewis acid sites catalyzed the isomerization of arabinose to xylose, thereby increasing the selectivity for production of furfural. Using H-Beta zeolite and arabinose as feed, they were able to obtain furfural yields of up to 73% compared with 44% when sulfuric acid was used as a catalyst. This system allowed for the production of furfural at high yields (62%) from corn fiber, a feedstock rich in arabinose. However, similar to other solid catalysts, H-beta deactivated with time on stream due to coke deposition on the catalyst.

To mitigate deactivation problems, other authors have used homogeneous catalysts in biphasic systems. Campos Molina *et al.*<sup>113</sup> used sulfuric acid with cyclopentyl-methyl-ether as the organic phase to achieve furfural yields over 90% from cardoon biomass. The presence of a biphasic system was necessary, as furfural yields were only 67% in water. In addition, the presence of NaCl increased the production of C<sub>5</sub> sugars from the hemicellulose and subsequent production of furfural, reducing the reaction times required to achieve the maximum furfural yields from 250 to 30 min.<sup>114</sup> Amiri *et al.*<sup>115</sup> treated rice straw using sulfuric acid and reported yields of furfural of up to 45% when using a monophasic system. Yields increased to 70% when using THF and NaCl to create a biphasic system. Another advantage of NaCl addition is that it increases the partition coefficient of the furfural into the organic phase, thereby improving yields.<sup>109,116</sup> Yang *et al.*<sup>117</sup> added a Lewis acid to promote the isomerization of the xylose to xylulose. By using THF as a solvent in a biphasic system, they reported furfural yields from corn stover (55%), pinewood (61%), switchgrass (56%), and poplar (64%). These yields are close to those achieved from pure xylan (66%).

Gurbuz *et al.*<sup>118</sup> proposed the use of *sec*-butylphenol (SBP) for continuous extraction of furfural during the reaction. NaCl was added to improve furfural partition into the organic phase. They reported furfural yields of up to 75% from corn stover, close to the yields reported from xylose (78%). Furfural concentrations in SBP were increased to over 5 wt% by successive additions of corn stover, with subsequent yields remaining over 70%. Such concentrations are over five times higher than those typically reported for production of furfural (<1 wt%), demonstrating the appeal of this method. However, due to the neutralization capacity of biomass, 0.25 M HCl was required when using corn stover, compared to 0.1 M HCl with pure xylose.

Alonso *et al.*<sup>119</sup> used GVL, an organic water-soluble solvent, to stabilize furfural and prevent its degradation. Use of GVL as a solvent allowed the use of lower sulfuric acid concentrations, which minimized the degradation of furfural in monophasic systems. The lower acid concentrations that are required when using GVL instead of pure water are once again thought to be due to the changing stabilization of the acidic proton relative to the transition state when the solvent is present.<sup>80</sup> In addition, because the boiling point of furfural is lower than that of GVL, furfural could be continuously removed by vaporization, increasing the yields to over 81% from corn stover. A yield of 87% was obtained using Mordenite when the furfural was left in solution.<sup>103,119</sup> When the lignin was removed from

corn stover by alkaline hydrogen peroxide (AHP) pretreatment, furfural yields of up to 96% were obtained from the pretreated corn stover using sulfuric acid in a monophasic GVL–water mixture after 30 min.<sup>119</sup> Longer reaction times led to furfural degradation, decreasing yield, but increasing the production of levulinic acid from the C<sub>6</sub> sugars. Zhang *et al.*<sup>120</sup> explored the option of using FeCl<sub>3</sub> as a catalyst while using GVL as solvent. They were able to obtain furfural yields close to 80% from corn cobs. They observed that water addition to GVL caused a reduction in the reaction rate, as previously reported.<sup>103</sup> However, the presence of a small amount of water decreased furfural degradation. As reported by Gurbuz *et al.*, a fraction of the furfural produced comes from the dehydration of C<sub>6</sub> sugars,<sup>103</sup> which can explain the low yields obtained from pure xylan (68.6%) compared with the cobs and pure xylose (86.5%).

A similar system has been described by Cai *et al.*<sup>121</sup> who used THF, a polar aprotic solvent that is thought to lead to similar kinetic effects to those observed for GVL.<sup>80</sup> They reported furfural yields of up to 87% from maple wood with sulfuric acid as a catalyst after 60 min at 443 K in a THF–water mixture. Under the same conditions, they reported the production of levulinic acid (40%) and HMF (21%) from the C<sub>6</sub> sugars.

Zhang *et al.*<sup>122</sup> reported the use of solid acid catalysts with ionic liquid [BMIM]Cl as a solvent for production of furfural. The yields obtained from biomass were low (17.5%) when using a combination of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and AlCl<sub>3</sub> at 433 K for 3 h to treat corn cobs. Higher yields were obtained from grass (26.8%) without the addition of AlCl<sub>3</sub> after 10 h at 443 K. These yields are lower than the value of 93.7% achieved from pure xylose, indicating the limitations of ionic liquids and solid acid catalysts when used with real feedstocks. Proteins, fatty acids, phospholipids, amino acids, anions and cations present in the biomass can deactivate the catalysts and/or interact with the solvents. Similar results were obtained using metal chlorides, such as AlCl<sub>3</sub>: yields of up to 84% can be obtained using xylose, but they decrease to 34%, 32% and 15% when using pine wood, grass or corn cobs, respectively.<sup>120</sup>

Van Buijtenen *et al.*<sup>123</sup> produced furfural by treating bagasse with a stream of gaseous HCl and steam, which continuously stripped the furfural, obtaining a yield of 60% and a concentration of 5.4 wt% furfural. This method reduces the vapor demands to less than 10 tons of steam per ton of furfural produced, compared to the more than 30 tons required in the commercial process.

With most systems, lower furfural yields have been reported when starting from lignocellulosic biomass compared to pure xylose. Kim *et al.*<sup>124</sup> compared the furfural yields obtained from hemicellulosic sugars from different biomass species and pure xylose. They observed that while 67% yield can be achieved from pure xylose, the yield decreases to 61%, 57%, 54% and 29% when the xylose is obtained from corn stover, switchgrass, poplar and pine, respectively. In this study, only the soluble fraction of biomass was used. Therefore, the sugars extracted were filtered to remove solid residues includ-

ing cellulose and lignin. The authors also observed that biomass-derived xylose reacted faster than crystalline xylose, which has also been observed by other authors.<sup>125</sup> This enhanced activity could be due to the presence of organic acids, such as formic or acetic acid, which can help catalyze the reaction. However, such acids tend to be less selective than strong acids and could contribute to the lower yields observed when using lignocellulosic biomass. The presence of salts, which has been shown by many authors to enhance dehydration reaction,<sup>114,126</sup> could also contribute to these increased reaction rates. At low pH, some salts, including AlCl<sub>3</sub>, can introduce Lewis acidity that promotes the isomerization of the pentoses to more reactive forms (xylulose from xylose or ribulose from ribose or arabinose).

### Levulinic acid

Glucose can be dehydrated to HMF, and HMF can then undergo rehydration to produce levulinic acid and formic acid (Fig. 1). Levulinic acid has the advantage of being both the final product in its reaction pathway<sup>127–130</sup> (Fig. 1) and being stable at the conditions at which it is produced. Moreover, this stability allows for the production of levulinic acid in monophasic systems, and more importantly in aqueous solutions. Finally, the conditions for producing levulinic acid from C<sub>6</sub> carbohydrates are relatively simple, as only an acid catalyst and moderate temperatures are required.<sup>131</sup>

Biofine plans to start its first commercial plant in 2015 for production of levulinic acid, with a capacity of 125 dry tons of waste per day. They had a pilot plant located in South Glens Falls, NY in 1998 and another one in Caserta, Italy which has since closed.<sup>132</sup> While the early estimations predicted a levulinic acid price of 0.10–0.15 \$ kg<sup>-1</sup>,<sup>133</sup> Biofine now hopes to be able to commercialize levulinic acid at a price around 1 \$ kg<sup>-1</sup> (commercial price is currently 3.5 \$ kg<sup>-1</sup>). The Biofine process utilizes solid waste (municipal, industrial and agricultural) as raw material, but it can be operated with a variety of lignocellulosic feedstocks, such as, hardwood or bagasse. In a first step, at high temperature (483 K) and short residence times (seconds), furfural (up to 50% yield) and HMF are produced. In a second step, at lower temperature (463 K) and longer reaction times (20 minutes), the HMF is converted to levulinic acid at high yields. They report overall levulinic acid yields of 75%. The process utilizes 1.5–3 wt% sulfuric acid as catalyst and 1–10 wt% biomass, which could yield product concentrations up to 2 wt% (Table 3). An important limitation of the process is that it requires the particle size of the biomass to be 0.5–1 cm to operate in a continuous flow mode. Furfural can be obtained as a by-product, with reported yields of up to 70%, and be separated before the second step by flashing.<sup>134,135</sup>

Hayes *et al.* carried out reaction kinetics studies for production of levulinic acid from lignocellulosic biomass using sulfuric acid as a catalyst (0.1–0.55 M), obtaining yields up to 63%.<sup>136</sup> The kinetic parameters they found were similar to other studies utilizing cellulose or glucose as raw material, which indicates that the presence of lignin and hemicellulose does not have a significant effect.<sup>136</sup> Chan *et al.*<sup>131</sup> optimized

the reaction conditions to produce levulinic acid from wheat straw. They were able to obtain yields of up to 68% at 482 K for 37 min using 0.35 M sulfuric acid and product concentrations of 1.2 wt%. They report that the acid concentration was the most important optimization parameter. Similar work has been conducted by Galletti *et al.* with various feedstocks.<sup>137</sup> By using microwave irradiation at 473 K for 0.25 h and 0.5 M HCl, they were able to obtain levulinic acid yields of over 70% from paper sludge (77.6%), olive tree pruning (71.3%) and wheat straw (73.5%). When using poplar sawdust, the levulinic acid yield increased from 52% to 72% when a pre-hydrolysis step was carried out, showing that it is easier to process sugars/cellulose than untreated lignocellulosic biomass. Cai *et al.* obtained the highest published concentration of levulinic acid (4.8% with 75% yield) when treating maple wood that had been pretreated hydrothermally.<sup>121</sup> The importance of this pre-hydrolysis step was demonstrated again by Galletti *et al.*<sup>138</sup> When they treated giant reed at 473 K for 1 h using 0.4 M HCl, they obtained yields of levulinic acid of up to 59%. However, when they carried out the reaction in two steps, heating the giant reed at 353 K for 2 hours and then increasing the temperature to 463 K for another hour, they obtained yields of up to 87.1%, the highest reported in the literature. Alternatively, addition of NaCl improved levulinic acid yields up to 77.4% when using wheat straw.<sup>139</sup>

While processes based on the use of homogeneous acids have been successful, separating the levulinic acid from the mineral acid is often the most expensive part of the process.<sup>140,141</sup> To alleviate this problem, researchers have studied heterogeneous catalysts for production of levulinic acid. The main challenge to using a heterogeneous catalyst is enabling its interaction with solid cellulose. To facilitate the conversion of cellulose using an acid catalyst (S<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub>-SiO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub>), Hongzhang *et al.*<sup>142</sup> employed steam pretreatment of rice straw to achieve 70% yields of levulinic acid. When coarsely ground solid biomass was used with the same catalyst but without any pretreatment, the yield decreased to 22.4%. When the rice straw was mechanically ground to 15–25 μm, the yield increased somewhat to 42%. Li *et al.*<sup>143</sup> used Amberlyst 15, but the yields achieved were low (15 g levulinic acid per kg of rice straw), with the main product being monomeric sugars. In addition, leaching of the catalyst into solution as sulfonic species took place at the reaction conditions (423 K).

Alonso *et al.*<sup>144</sup> proposed the production of levulinic acid in water by conventional methods, but they employed a subsequent extraction using alkylphenols (Fig. 6). The alkylphenol extracts the levulinic acid leaving the mineral acid in the aqueous phase, which can be directly reutilized with minor loss in activity (*e.g.*, the levulinic acid yield decreased from 55% to 46%). While similar initial yields were obtained from cellulose and corn stover, the loss of catalytic activity was more pronounced in the presence of lignin. Additional sulfuric acid was required to maintain yields when using lignocellulosic biomass, presumably due to acid neutralization by non-cellulosic biomass fractions. The main advantage of this separation is that once the levulinic acid is extracted, it can be recovered

by distillation or it can be converted into the fuel precursor, GVL, without further separation or purification.

### Simultaneous production of furfural and levulinic acid

Co-production of furfural and levulinic acid is a target when working with lignocellulosic biomass and producing dehydration products. Biofine reported the production of furfural at 70% yield in a first step, and production of levulinic acid at 75% yield in a second step after flashing off the furfural. Dussan *et al.*<sup>145</sup> studied the reaction kinetics for co-production of furfural and levulinic acid using Miscanthus as raw material. The maximum yields were achieved when the process was separated into two stages. In the first step, furfural is produced at 27% yield at 458 K and in 0.5 M sulfuric acid, while in the second step the temperature is increased to 473 K to produce levulinic acid at 72% yield. Alonso *et al.* produced furfural and levulinic acid simultaneously in a single reactor by using GVL as solvent. It has been reported that GVL can solubilize the biomass while increasing acid-catalyzed hydrolysis and dehydration reaction rates without increasing furanic product degradation.<sup>146,147</sup> At 443 K, Alonso *et al.*<sup>119</sup> obtained yields of furfural and levulinic acid of up to 56% and 61%, respectively, from corn stover with 0.1 M sulfuric acid in 80 wt% GVL and 20 wt% water in 1.5 hours. The advantage of this system is that furfural can be separated from the levulinic acid by distillation, or both molecules can be converted to GVL, itself a fuel precursor.<sup>4</sup> Other solvents, such as THF, can be used with similar results. Cai *et al.*<sup>121</sup> reported the co-production of furfural and levulinic acid at 86% and 40% yield

from maple wood, respectively, using THF–water as a solvent (3 : 1 ratio) at 443 K for 1 h using 1 wt% H<sub>2</sub>SO<sub>4</sub>. In addition, they reported the production of HMF at 21% yield (Tables 2–4). Longer residence times improved the levulinic acid yields while decreasing the yields of furfural and HMF. The same trend was observed by Campos-Molina *et al.*<sup>113</sup> In water, the degradation of furfural is rapid and coproduction is not a viable option. However, in the presence of cyclopentyl methyl ether, furfural is more stable and levulinic acid yields of up to 48% can be obtained while maintaining 90% furfural yields. Levulinic acid yields are limited because the presence of the organic solvent decreases the reaction rate. For example, in monophasic systems, levulinic acid yields of up to 65% were achieved in 120 min, whereas in the presence of the organic solvent, levulinic acid yields were only around 48% after 240 min. In both cases, NaCl is added to improve the production rate of levulinic acid.<sup>139</sup>

### Hydroxymethylfurfural

Many studies have focused on the production of HMF from glucose or fructose, but few studies have successfully produced this compound from real biomass.<sup>148</sup> Binder *et al.*<sup>149</sup> studied the production of HMF, the precursor to levulinic acid, directly from biomass. They processed several biomass sources in the presence of *N,N*-dimethylacetamide, LiCl, CrCl<sub>2</sub> and ionic liquid [EMIM]Cl at 413 K, obtaining yields to HMF of 16% (corn stover), 19% (pine sawdust) and 16% (AFEX™ corn stover). When HCl was added to the corn stover, the HMF yield increased to 48%. This value corresponds to the highest HMF

**Table 2** Conversion of untreated lignocellulosic biomass to furfural. The indices in the co-product column refer to processes producing multiple dehydration products. See corresponding yields in Tables 3 and/or 4

Feedstock	<i>T</i> (K)	Solvent	Time	Catalyst	Product concentration (wt%)	Furfural yield (%)	Co-product	Source
Corn cobs	453/493	Water	3–7 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.5%	98%		90
Cardoon	443	CPME, water, NaCl	0.5 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.5%	98%	A	113
Cardoon	443	Water, NaCl, monophasic	0.5 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.5%	67%	B	113
Corn Stover	443	GVL, water, monophasic	2 h	Mordenite	0.9%	87% <sup>a</sup>		119
AHP corn stover	443	GVL, water, monophasic	0.5 h	0.025 M H <sub>2</sub> SO <sub>4</sub>	0.9%	96% <sup>a</sup>		119
Maple wood	443	THF, water monophasic	1 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.5%	86	C	121 <sup>b</sup>
Rice straw	423	Water	5 h	0.05 M H <sub>2</sub> SO <sub>4</sub>	0.3%	39%		115
Rice straw	423	THF, water, NaCl	5 h	0.05 M H <sub>2</sub> SO <sub>4</sub>	0.23/(0.46)%	70%		115
Corn stover	443	<i>sec</i> -Butylphenol, water, NaCl	0.25 h	0.25 M HCl	5.3%	75%		118
Corn stover	433	THF, water, NaCl	1 h	0.025 M AlCl <sub>3</sub>	0.2%	55%		117
Pinewood	453	THF, water, NaCl	0.5 h	0.025 M AlCl <sub>3</sub>	0.2%	61%		117
Switchgrass	433	THF, water, NaCl	1 h	0.025 M AlCl <sub>3</sub>	0.2%	56		117
Poplar	433	THF, water, NaCl	1 h	0.025 M AlCl <sub>3</sub>	0.2%	64		117
Bagasse	431	Gas HCl, steam	6.3 h	2 wt% HCl	10.1	60%		123
Corn stover	443	GVL, water, monophasic	1.5 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.6%	56%	G	119
Corn cob	458	GVL, water monophasic	1.7 h	0.6 wt% FeCl <sub>3</sub>	0.45%	79.6% <sup>a</sup>		120
Corn fiber	433	GVL, water monophasic	2 h	0.05 M H <sub>2</sub> SO <sub>4</sub>	0.7%	56%		105
Corn fiber	433	GVL, water monophasic	2 h	3.75 wt% H-Beta	0.8%	65%		105
Corn stover	338	Water, dichloromethane	18 h	12 M HCl	0.2%	40%		208
Solid waste	493	Water	Seconds	0.1–0.3 wt% H <sub>2</sub> SO <sub>4</sub>	0.1–1%	73.6%	D	209
Grass	433	[BMIM]Cl	0.16	NKC-9	0.07	24.3	E	122

<sup>a</sup> Part of the furfural may come from C<sub>6</sub> sugars and not C<sub>5</sub> sugars. <sup>b</sup> While this article was in press, this process was improved to be able to simultaneously produce furfural and HMF at yields of 95% and 51%, respectively, from maple wood. Furfural and HMF were obtained at concentrations of 0.5 wt% and 0.8 wt%, respectively, after treatment of 5 wt% maple wood for 60 min at 440 K with 0.8 wt% FeCl<sub>3</sub> in 4 : 1 THF : water. C. M. Cai, N. Nagane, R. Kumar and C. E. Wyman, *Green Chem.*, 2014, **16**, 3819–3829.

**Table 3** Conversion of untreated lignocellulosic biomass to levulinic acid. The indices in the co-product column refer to processes producing multiple dehydration products. See corresponding yields in Tables 2 and/or 4

Feedstock	T (K)	Solvent	Time	Catalyst	Product concentration (wt%)	Levulinic acid yield (%)	Co-product	Source
Cardoon	443	Water/NaCl	2 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.7	65	B	113
Cardoon	443	CPME, water, NaCl, Biphasic	4 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.5	48	A	113
Solid waste	493/463	Water	Seconds/minutes	0.3 M H <sub>2</sub> SO <sub>4</sub>	0.1–2%	75%	D	134,135
Bagasse	423	Water	8 h	0.55 M H <sub>2</sub> SO <sub>4</sub>	2%	63%		136
Wheat straw	482	Water	0.6 h	0.35 M H <sub>2</sub> SO <sub>4</sub>	1.3%	68%		131
Paper sludge	473	Water	0.25 h	0.5 M HCl	4%	78%		137
Wheat straw	473	Water	0.25 h	6 wt% NbP	0.6%	25%		137
Giant reed	353/463	Water	2/1 h	0.4 M HCl	1.6%	87%		138
Corn stover	428	Water, alkylphenol	6 h	0.5 M H <sub>2</sub> SO <sub>4</sub>	1.8%	55%		144
Miscanthus	458/473	Water	12–15 s/ 15–30 min	0.5 M H <sub>2</sub> SO <sub>4</sub>	2%	72%		145
Corn stover	443	GVL, water, monophasic	1.5 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	1.1%	61%	G	119
AHP corn stover	443	GVL, water, monophasic	1 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.8%	58%		119
Maple wood	443	THF, water, monophasic	1 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.5%	40%	C	121
Pretreated maple wood	473	Water	0.66 h	0.15 M H <sub>2</sub> SO <sub>4</sub>	4.8%	75%		121
Rice straw (15–25 um)	473	Water	0.17 h	S <sub>2</sub> O <sub>8</sub> /ZrO <sub>2</sub> –SiO <sub>2</sub> –Sm <sub>2</sub> O <sub>3</sub>	0.7%	42%		142
Pretreated rice straw	473	Water	0.17 h	S <sub>2</sub> O <sub>8</sub> /ZrO <sub>2</sub> –SiO <sub>2</sub> –Sm <sub>2</sub> O <sub>3</sub>	1.2%	70%		142
Corn stover	373/463	Water Dichloromethane	3 h/20 min	12 M HCl/—	0.1 wt%	81%	F	154

**Table 4** Conversion of untreated lignocellulosic biomass to HMF. The indices in the co-product column refer to processes producing multiple dehydration products. See corresponding yields in Tables 2 and/or 4

Feedstock	T (K)	Solvent	Time	Catalyst	Product concentration (wt%)	HMF yield (%)	Co-product	Source
Maple wood	443	THF, water, monophasic	1 h	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.3%	21%	C	121 <sup>a</sup>
Pine	413	[EMIM]Cl	5 h	N,N-Dimethylacetamide, LiCl, CrCl <sub>2</sub>	0.6%	19%		149
Corn stover	413	[EMIM]Cl	6 h	N,N-Dimethylacetamide, LiCl, CrCl <sub>2</sub>	0.4%	16%		149
Corn stover	413	[EMIM]Cl	2 h	N,N-Dimethylacetamide, LiCl, CrCl <sub>2</sub> , HCl	1.3%	48%		149
Grass	433	[BMIM]Cl	0.16 h	NKC-9	0.14%	22.6	E	122
Rice straw	453	Water, butanol, propanol	3 h	0.5 wt% SA	0.3%	20		115
Poplar	453	Water, THF NaCl	0.5 h	0.1 M HCl	0.1%	21%		150
Pinewood	433	Water, THF, NaCl	1 h	0.025 M AlCl <sub>3</sub>	0.2%	42%		117
Bagasse	393	[BMIM]Cl	5 min	20 mol% Zr(O)Cl <sub>2</sub> /CrCl <sub>3</sub>	0.5%	42%		152
Corn stover	373/373	Water Dichloromethane	3 h/30 s	12 M HCl/—	0.1%	69%	F	154

<sup>a</sup> While this article was in press, this process was improved to be able to simultaneously produce furfural and HMF at yields of 95% and 51%, respectively, from maple wood. Furfural and HMF were obtained at concentrations of 0.5 wt% and 0.8 wt%, respectively, after treatment of 5 wt% maple wood for 60 min at 440 K with 0.8 wt% FeCl<sub>3</sub> in 4 : 1 THF : water. C. M. Cai, N. Nagane, R. Kumar and C. E. Wyman, *Green Chem.*, 2014, **16**, 3819–3829.

concentration (1.3 wt%) obtained directly from lignocellulosic biomass. These yields are lower than those obtained from cellulose (54%), glucose (80%) and fructose (92%). Zhang *et al.* reported HMF yields up to 22.5% along with 24.3% furfural from grass using [BMIM]Cl as a solvent and H<sub>3</sub>P<sub>12</sub>O<sub>40</sub> as a solid acid catalyst.<sup>122</sup> However, as in all the cases where ionic liquids are used, separation of the furans from the reaction solvent is an important challenge. Ethyl acetate proved to be an interesting extraction solvent, with extraction yields of over 95%. However, the low concentration of the products makes this extraction economically prohibitive in view of the high energy requirement of the distillation step to recover the product.

Amiri *et al.*<sup>115</sup> employed a biphasic system for production of HMF (Fig. 6). Butanol or propanol were used as the organic phase and HMF yields of up to 23% at 76% conversion were achieved. However, only 70% of the HMF produced was extracted into the organic phase, with the rest remaining in the aqueous phase. Under similar conditions, but using THF as a solvent and adding NaCl to create a biphasic system at 453 K, Yang *et al.*<sup>150</sup> reported HMF yields of up to 26% from poplar. While the presence of a Lewis acid such as AlCl<sub>3</sub> increased the HMF yield from 12% (HCl) to 61% (AlCl<sub>3</sub>) when using glucose, it did not have a significant effect in the case of poplar (21% HMF yield with HCl and no salt), which was

significantly different from the yields obtained from cellobiose (58%) and glucose (65%). However, when using pinewood, the HMF yield increased to 35% (453 K) and 42% (433 K).<sup>117</sup> These yields are comparable to the overall yields that can be obtained in a two-stage process to produce sugars followed by HMF production in a biphasic system. Overall, HMF yields from corn stover after biomass hydrolysis led to overall yields of 47% HMF when GVL was used as a solvent, when there was separation of the aqueous phase, and when there was dehydration in the presence of an alkylphenol organic phase and AlCl<sub>3</sub>.<sup>78</sup> Similarly, when soluble C<sub>6</sub> carbohydrates produced using the previously discussed mechanocatalytic process were treated in a similar biphasic system with AlCl<sub>3</sub>, yields of approximately 55% were obtained.<sup>151</sup>

Dutta *et al.*<sup>152</sup> converted sugarcane bagasse into ethoxy-methylfurfural (EMF), a fuel additive, by using metal chlorides in DMA-LiCl and ionic liquids ([BMIM]Cl) with ethanol. In a first step, they obtained HMF yields of 42% from sugarcane bagasse in the presence of Zr(O)Cl<sub>2</sub>/CrCl<sub>3</sub> and using [BMIM]Cl as a solvent. HMF was converted to EMF when ethanol was added to the system.

Mascal *et al.*<sup>153,154</sup> proposed an approach for conversion of lignocellulosic biomass to produce an intermediate product, 5-hydroxychloromethylfurfural (CMF). The chloro functionality can then be replaced to yield various products including HMF, levulinic acid, or ethyl levulinate. This process, which uses concentrated HCl and dichloroethane, can produce HMF at a yield of 69% from corn stover. Alternatively, CMF can be converted to levulinic acid at an overall yield of 81%. These yields are similar to those achieved with cellulose and glucose, indicating that this method is relatively immune to the effects of biomass impurities. If the CMF is heated in the presence of an alcohol, levulinate esters can be produced at 75% yield. While the isolated yields are high, the separation of the CMF and recovery of the HCl have not been studied in detail. The xylan present in the corn stover can be converted into furfural, but at low yields (40%).<sup>155</sup>

## 4. Other chemical opportunities

### Combined depolymerisation and hydrogenation to polyols

Sorbitol, which can be produced by hydrogenation of C<sub>6</sub> sugars, is an established platform molecule that is used as a sweetener in the food industry or a thickener in the cosmetics industry. Xylitol, the C<sub>5</sub>-analogue of sorbitol, is produced by

hydrogenation of xylose and is used as a sorbitol substitute in the food additive industry. More recently, sorbitol and xylitol have been suggested as a potential entry intermediates for production of fuels such as alkanes, aromatics or hydrogen.<sup>156–158</sup>

Various studies have combined acid-catalyzed hydrolysis with metal-catalyzed hydrogenation to convert cellulose to sorbitol. Typical reactions have used a metallic ruthenium catalyst in combination with an acid catalyst for hydrolysis. Many of the hydrolysis systems that have been used are those that we have discussed in Section 2 of this review and include mineral acid hydrolysis with H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>,<sup>159</sup> mechanocatalytic acid hydrolysis,<sup>160</sup> and ionic liquid hydrolysis.<sup>161</sup> However, bifunctional catalysts specifically designed for combined hydrolysis and hydrogenation have also been proposed.<sup>162</sup> Similar experiments using sulfuric acid and Ru/C have also been carried out with beech-extracted xylan to produce xylitol.<sup>163</sup>

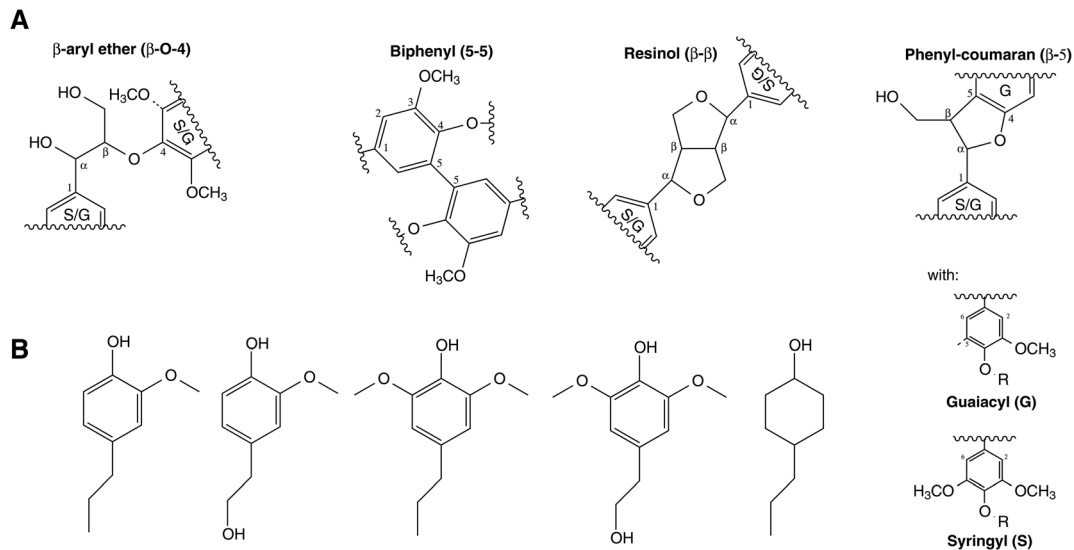
Few studies have investigated the production of sorbitol or xylitol from untreated lignocellulosic biomass. Li *et al.* produced xylitol from solutions of xylose and xylose oligomers produced from maple wood by using a Rh/C catalyst combined with sulfuric acid or oxalic acid as the hydrolysis catalyst.<sup>158</sup> Slightly above 50% carbon selectivity of xylitol was obtained from a sugar solution obtained by oxalic acid-catalyzed hydrolysis from maple wood after hydrogenation, leading to concentrations of xylitol of over 20% (Table 5). Robinson *et al.* were the only authors to target combined hemicellulose and cellulose conversion to xylitol and sorbitol, respectively, from various forms of lignocellulosic biomass, including oak and corn fiber.<sup>164</sup> They obtained sorbitol and xylitol yields of about 65–76% after simultaneous hydrogenation and hydrolysis in the presence of 0.7 wt% phosphoric acid and Ru/C at 460 K, with product yields around 5% depending on the conditions and biomass used (Table 5).

### Lignin monomers

Lignin is the third major fraction of biomass after cellulose and hemicellulose, and generally accounts for 15–30% of its weight. However, due to its lower oxygen content (27–30 wt% oxygen in lignin *versus* 49 wt% in cellulose), it accounts for about 40% of the biomass heating value.<sup>165</sup> Because of this, and because of the phenolic functionalities of its various monomers (Fig. 7), this fraction has been the subject of numerous chemical conversion studies. In particular, many researchers have focused on developing innovative chemistry to selectively break the most common chemical bonds present in lignin, including β-O-4, 5-5, and 4-O-5 linkages (Fig. 7)

**Table 5** Conversion of untreated lignocellulosic biomass to polyols (sorbitol and xylitol). Backslashes delimit conditions at separate processing stages

Feedstock	T (K)	Solvent	Time	Catalyst	Product concentration (wt%)	Polyol yield (%)		
						Xylitol	Sorbitol	Source
Maple wood	433/413	Water	30 min/N.R.	0.5 wt% oxalic acid/5 wt% Ru/C	24%	78%	5.6%	158
Oak	463	Water	4.3 h	0.7 wt% H <sub>3</sub> PO <sub>4</sub> and 0.5 wt% Ru/C	4.7%	65%		164
Acetone extracted oak	460	Water	3 h	0.7 wt% H <sub>3</sub> PO <sub>4</sub> and 0.5 wt% Ru/C	5%	72%		164
Corn Fiber	440	Water	4 h	0.7 wt% H <sub>3</sub> PO <sub>4</sub> and 0.5 wt% Ru/C	2.8%	76%		164



**Fig. 7** (A) Bonds comprising more than 10% of lignin linkages.<sup>165</sup> (B) Main lignin monomers that have been reportedly produced from lignin at yields higher than 10 wt%.

through the study of model compounds. There have been many such studies and they are beyond the scope of this review, which covers the conversion of real lignocellulosic biomass. However, these model compound studies have been extensively covered in a recent review on the chemical transformation of lignin.<sup>165</sup> In contrast, there have been fewer studies using real lignocellulosic biomass, and the most common approach in this respect has been to use hydrogenolysis to recover lignin monomers—typically in the form of cyclohexyl or phenyl propane and their derivatives. The work of Hibbert and coworkers, published in the 1940s, is an early example of this approach.<sup>166,167</sup> In a typical experiment, solvent-extracted maple wood was reacted in the presence of a copper chromite catalyst in dioxane at 280 °C with high hydrogen pressures (200 bar). After 20 h, a 12% yield of 4-propylcyclohexanol and a 6% yield of 3-cyclohexyl-1-propanol were obtained. About 20 years later, Pepper *et al.*<sup>168</sup> treated solvent-extracted spruce at 195 °C for 5 h in the presence of Rh/C and 30 bar H<sub>2</sub> in dioxane to obtain up to 34% monomer yield from spruce, including 11% propyl guaiacol (2-methoxy-4-propylphenol) and 20% guaiacyl propanol (4-(3-hydroxypropyl)-2-methoxy-phenol). More recently, Azadi *et al.* used a similar method with water as a solvent to produce lignin-derived solvents containing mostly propyl guaiacol and/or propyl syringol (2,6-dimethoxy-4-propylphenol) from poplar.<sup>169</sup> In an interesting example of process integration, this solvent was used as the organic phase in the biphasic reactions to produce furfural, 5-HMF and levulinic acid from biomass. Yan *et al.* improved on these previously developed hydrogenolysis methods by adding phosphoric acid when treating benzene-extracted birch in a water–dioxane mixture in the presence of noble metal catalysts supported on carbon and 4 MPa H<sub>2</sub> at 473 K.<sup>170</sup> With this method, they obtained up to 46% monomer yields from the “C<sub>9</sub> units” of lignin, including up to 10% propyl guaiacol, 35% propyl syringol, 15% syringyl

propanol (2,6-dimethoxy-4-(3-hydroxypropyl)phenol), and 12% dimers. It was unclear from their work how yield from C<sub>9</sub> units translates to a yield by weight or a carbon yield. They were able to convert these molecules to C<sub>9</sub>–C<sub>18</sub> cycloalkanes using Pd/C, 5% H<sub>3</sub>PO<sub>4</sub> and 4 MPa H<sub>2</sub> in water at 523 K.

Although the studies mentioned above have successfully converted lignin, these studies did not simultaneously upgrade all three biomass fractions. A recent study has addressed this simultaneous conversion by treating ashtree in the presence of a Ni-W<sub>2</sub>C/AC catalyst in water at 508 K.<sup>171</sup> A 76% yield of diols (mostly ethylene glycol) was obtained from the hemicellulose and cellulose portions of biomass along with a 36% yield of lignin monomers (mostly syringyl propanol and propyl syringol).

Various studies have investigated the conversion of isolated forms of lignin, notably, those forms obtained as a side product of pulp and paper processes such as Kraft lignin, sulfite lignin or organosolv lignin. Similar to pure cellulose or isolated hemicellulose, the conversion of these products is not necessarily comparable to converting lignin in an integrated biomass conversion process. Therefore, we have chosen to not include a thorough review of these processes in this work; rather, we limit our discussion to the principal differences associated with the upgrade of these isolated lignin fractions compared to the previously discussed upgrading of lignin from untreated biomass. In-depth reviews covering the conversion of these streams have been done by Pandey *et al.*<sup>172</sup> and Zakzeski *et al.*<sup>165</sup>

Contrary to what is often the case for pure cellulose or isolated hemicellulose, the conversion of lignin isolated from pulp and paper processes can lead to lower yields. This behavior is notably the case for Kraft lignin, which is isolated by treatment with sodium hydroxide and sodium sulfide.<sup>173</sup> The harsh pulping conditions that are required to create a highly purified cellulose stream can lead to breakage of the more labile  $\beta$ -O-4 linkage, and to the formation of highly stable

carbon-carbon linkages by radical coupling, which can significantly hinder further upgrading.<sup>174</sup> This effect is illustrated by the difference in yields obtained for Kraft lignin and benzene-extracted poplar. Kraft lignin treated at 473 K for 4 h in the presence of Pd/C and hydrogen in an ethanol water mixture yielded about 2 wt% ethyl and propyl guaiacol.<sup>175</sup> In comparison, benzene-extracted pine treated at the same temperature for the same amount of time in water in the presence of the same catalyst and hydrogen produced a monomer yield of 26%, including 16% syringyl propanol and 5% guaiacyl propanol.<sup>170</sup> The oxidation of Kraft lignin catalyzed by polyoxometalates or transition metal salts in the presence of methanol has led to total yields of vanillin and methyl vanillate of about 6–7 wt%.<sup>174,176,177</sup> The methanol serves to prevent repolymerization by forming an ester with the vanillic acid. Oxidation of Kraft lignin in the presence of base led to similar yields.<sup>178</sup> Sulfite lignin also contains sulfur but is produced by treatment with sulfurous acid and sulfites. It has been used as a raw material for the production of vanillin by Borregard®. They have reported yields of up to 7.2 wt% from liginosulfonates obtained by molecular oxidation using copper and cobalt catalysts.<sup>179</sup> Despite these relatively low yields, to this day vanillin remains the only monomeric product that has been commercially produced from lignin.<sup>172</sup>

Organosolv lignin is removed using solvents and is often better conserved than Kraft lignin. Using organosolv lignin, Roberts *et al.* have reported producing lignin-derived oil using NaOH-catalyzed depolymerization with boric acid supplementation at yields close to 85%.<sup>180</sup> However, they report limited yields of actual identifiable products, with the highest reported monomer yields (mostly guaiacyl and syringyl derivatives) around 15 wt%.<sup>180</sup> In similar work, a base-catalyzed depolymerization process was patented, in which Kraft or organosolv lignin in an ethanol solution was treated at 540–560 K in the presence of NaOH.<sup>181</sup> Following depolymerization, the resulting oil was treated in the presence of various hydrocracking catalysts, such as NiW/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or CoMo/Al<sub>2</sub>O<sub>3</sub>. The authors report lignin conversion close to 100% and up to 73% “gasoline” yield. However, yields of individual products are not reported.

The difficulty of obtaining high yields of a given product from lignin is largely linked to the diversity of chemical bonds and functionalities. Due to this inherent limitation, lignin has been suggested as a possible source of materials and material additives, including additives to cement, precursors for producing carbon fibers or co-polymerization additives for thermoplastics. These processing routes have recently been reviewed,<sup>182</sup> and they fall outside of the scope of this review, which is focused on targeted chemical upgrading.

## 5. Economic trade-offs between processes

### Sugars production

Concentrated acid processes can reach close to quantitative yields for production of sugars, with product concentrations

**Table 6** Feedstock, catalyst, solvent and product prices associated with biomass conversion

Name	Price [\$ per ton]	Market size [ton per year]	Source
<i>Feedstock</i>			
Biomass	60–100		184
<i>Catalyst/solvents</i>			
Enzyme	10 000 (25–75) <sup>a</sup>		29,192
Sulfuric acid	35		78
HCl	200		186
Ionic liquids	3000–50 000		186,187,210
GVL	1000 <sup>b</sup>		188
<i>Products</i>			
Corn dextrose	440	150 million	185,198
Furfural	1000–1750	250 000	<sup>c</sup>
HMF	1000 <sup>b</sup>	n/a	211
Levulinic acid	600–5000	500	<sup>c</sup>
Formic acid	600–750	250 000	<sup>c</sup>
Sorbitol	880–970	800 000 <sup>d</sup>	212
Xylitol	1450–1630	200 000 <sup>d</sup>	196
Lignin monomers	n/a	n/a	

<sup>a</sup> Typical price per ton of biomass. <sup>b</sup> Minimum selling price. <sup>c</sup> Obtained from: “Initial findings for furanic derived Chemicals: Evaluation of technology Commercialization Opportunity” Report for compiled by Clean Energy Trust for the Wisconsin Alumni Research Foundation, August 2012. <sup>d</sup> Obtained from <http://www.starch.dk>.

over 70 wt%. However, acid recovery is a key factor in their economic success. Virdia® has been able to renew interest in this approach because it has proposed a novel way to recover the HCl.<sup>183</sup> Ionic liquid<sup>83</sup> and GVL-based processes<sup>78</sup> offer a similar trade-off. They can reach sugar yields of around 70–90% and in the case of the GVL process, sugar concentrations close to 13 wt%. However, energy and capital must be expended to recover the ionic liquids or GVL, without which the process would be uneconomical.

This trade-off can be illustrated by the comparing the cost of various feedstocks (Table 6). Biomass cost is estimated to be between \$60 and \$100 per dry ton.<sup>184</sup> If sugars are produced at 100% yield, then their cost in terms of biomass would be \$90–150 per ton. This value compares with the current price of corn dextrose, which is around \$440 per ton.<sup>185</sup> Although it can be argued that corn dextrose is not as sustainable as cellulosic sugars and that sugars are not the final desired product, in practice new cellulosic sugar processes must often compete with the price of corn dextrose as they enter the bio-fuels or bioproducts market. This comparison illustrates that low-yield processes (*e.g.*, around 50% glucose) are unlikely to be profitable. In contrast, in high-yield processes, the use of chemicals must be limited. The price of ionic liquids is estimated to be around \$10 000 per ton (although some studies have reported prices as low as about \$3000 per ton for imidazolium-based ionic liquids and as low as \$1240 for other types of ionic liquids that are not typically used for biomass conversion could be attained using a sufficient production scale and reasonably priced raw materials),<sup>186,187</sup> compared to \$35 per ton for sulfuric acid and about \$200 per ton for HCl.<sup>78,186</sup> Studies have estimated that GVL can be produced for about



\$1000 per ton.<sup>188</sup> In comparison, enzyme costs have been estimated to be in the range of \$25–75 per ton of biomass treated<sup>29,184</sup> (Table 6). Therefore, to limit catalyst costs to a similar value of \$50 per ton of biomass, losses must be limited to 500–150 kg acid, 5 kg ionic liquid or 50 kg GVL per ton of biomass. However, a key difference for GVL is that it can be produced from biomass itself. In fact, production of GVL from dehydration by-products such as HMF, furfural or levulinic acid produced during the depolymerization process to sugars could make-up for solvent losses.<sup>78</sup> Another aspect to consider is the sustainability of these various solvents and/or catalysts. Although these aspects are more difficult to quantify, it is likely that the production of ionic liquids or other inorganic chemicals will be less sustainable than enzymes or biomass-derived solvents, which can be produced from biomass itself.

In comparison, chemical costs are less of a concern for dilute acid or pure water processes. However, these processes face trade-offs between yield and product concentration. As glucose yields decrease to values close to 50%, the cost contribution of the biomass alone approaches the cost of corn dextrose. In parallel, several studies have found that in the case of a bioethanol process, ethanol concentrations prior to distillation of higher than 4 wt% must be attained to make the process economically feasible.<sup>189–191</sup> Production of a 4 wt% ethanol solution requires an initial sugar solution of at least 8 wt%. This requirement is confirmed by industrial scenarios proposed by NREL, which assume 10 wt% sugar solutions leading to 5 wt% ethanol solutions.<sup>184,192</sup> To our knowledge, no dilute acid or pure water process has been able to reach these metrics. High-yield (>80%) flow-through reactions produce sugar solutions below 4 wt%.<sup>53</sup> Two-stage dilute acid wood hydrolysis produced solutions above 10 wt% but with glucose yields around 50%. When using only pure water and high temperatures, the Renmatix® Plantrose™ process was able to reach 66% glucose yields but only at around 2–3% product concentrations.<sup>65</sup> In such processes, there appears to be a trade-off between achieving the high heating rates necessary for the short residence time (seconds or less) translating to high yields, and employing the high solid concentrations necessary to obtain high product concentrations.

Of course, sugars are often not the final product that is desired. Even though these depolymerization processes will likely have to compete with corn dextrose prices, they could find higher revenues by integrating subsequent chemical upgrading processes (see below) and/or biological conversion processes (Fig. 8A).

### Furans and their derivatives

One advantage of targeting dehydration products over sugars is the possibility of increased revenue due to the potentially higher price that can be obtained for these products (Table 6). In addition, furfural, HMF and levulinic acid have been proposed as building blocks to produce chemicals currently made from petroleum (Fig. 8B–D). Such molecules would be considered green and sustainable alternatives to currently used

petroleum-derived products. While premium prices or government discounts may be applied, in order to be used at commercial scale, the price for these chemicals must be close to \$1000 per ton (over twice the price that can be obtained for sugars). Currently, only furfural is produced at that price, making it the most important biomass-derived dehydration chemical. However, the furfural market is saturated with almost all of it being used to produce furfuryl alcohol. It is expected that renewed efforts in biomass processing research can bring the price under \$1000 per ton, thereby expanding the market significantly. For example, furfural can be converted into furan and tetrahydrofuran, which can be used to produce 1,4 butanediol—an important polymer precursor (Fig. 8B).<sup>99</sup> This route was abandoned because of the high price of furfural. Other opportunities for low-cost furfural could include the production of furoic acid, maleic acid or maleic anhydride, which can be used to produce polyesters and resins. Again, if its production price was sufficiently low (~\$500 per ton), then furfural could be converted into methyl-tetrahydrofuran, a component of the series P-fuel. C<sub>6</sub> sugar dehydration products, HMF and levulinic acid are not yet on the market because of the high cost of production. Once the price becomes lower than \$1000 per ton, levulinic acid could be used to produce levulinic esters or  $\gamma$ -valerolactone and enter in the biofuels market (Fig. 8C).<sup>193</sup> In addition, levulinic acid can be used to produce ketals, and be used as solvents, lubricants or plasticizers, or to produce polyols, thermosets, and thermoplastics. In addition, it can be used to produce fine chemicals such as  $\delta$ -aminolevulinic acid or diphenolic acid. While the market for specialty chemicals is limited, the prices for these products are higher than those for commodity chemicals. The specialty market could therefore be an interesting entry point for levulinic acid production technologies, enabling further development. HMF has been the focus of much attention in part because it can be converted to furandicarboxylic acid, which can be used to replace terephthalic acid in polyester production by yielding polyethylene furandicarboxylate (PEF) instead of polyethylene terephthalate (PET).<sup>194</sup> If this opportunity becomes economical, demand for HMF would increase significantly. Other products that could be produced from HMF include diformylfuran and bishydroxymethylfurfural, which could be used as polymer precursors (Fig. 8D).<sup>194</sup> As is the case with furfural, if the price of HMF can be reduced sufficiently, there is the potential to produce biofuels such as dimethylfuran.

### Hydrogenation products

In contrast to dehydration products and similar to sugars, sorbitol has a market that is much larger than for furans, and therefore prices can be expected to remain close to those reported here.<sup>195</sup> The large market for sorbitol also explains why its price is not as high as for other sugar derivatives (Table 6). Because of this large market, the price of sorbitol is also lower than for some of the other commodity chemicals that can be produced from sugars, such as xylitol, which is not as widely used as sorbitol and commands a higher price.<sup>196</sup>

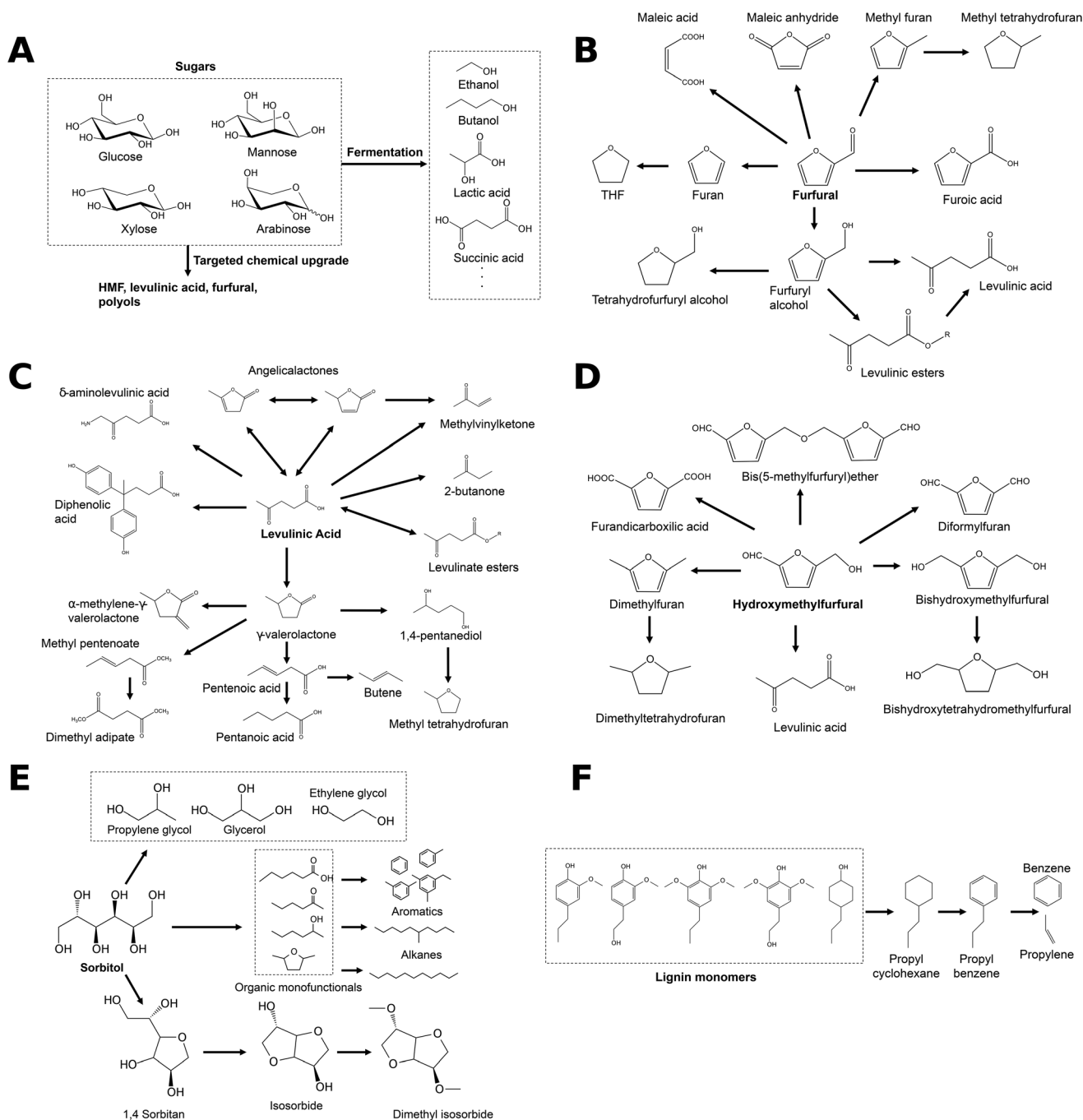


Fig. 8 Potential upgrading routes for (A) sugars, (B) furfural, (C) levulinic acid, (D) HMF, (E) sorbitol and (F) lignin monomers.

Therefore, sorbitol provides a good example of a commodity chemical that can be produced from glucose with a well-established market and market price. Sorbitol and xylitol are mainly used as artificial sweeteners but, in the context of increased interest in sustainability, they are increasingly being explored as sources of green fuels and chemicals (Fig. 8E). A conversion route for sorbitol to various fuels and chemicals was proposed wherein sorbitol is deoxygenated over a PtRe catalyst to produce organic monofunctionals.<sup>156,197</sup> These monofunctionals can then be upgraded through various routes to either

produce aromatic hydrocarbons or alkanes. In addition, sorbitol can also be used to produce commodity polyols such as propylene glycol, glycerol and ethylene glycol. Alternatively, sorbitol can be converted to sorbitan and then isosorbide, which can then be used to produce dimethyl isosorbide by esterification, an industrial solvent, or be used as a polymer precursor.<sup>198</sup>

High yields of lignin monomers can also be produced by hydrogenation. There is no real market for the guaiacyl or syringyl derivatives produced from lignin. However, these mono-

mers can be further hydrodeoxygenated to propyl cyclohexane, which could be used as a drop-in fuel. Propyl cyclohexane could also be dehydrogenated and then cracked to produce benzene and propylene, which are two major commodity chemicals. Whether these routes are pursued will depend on whether lignin can be upgraded and valorized efficiently in tandem with the other fractions of biomass.

## 6. Conclusions and future perspectives

Lignocellulosic biomass is an attractive source of renewable carbon for producing some of the fuels and chemicals that are currently made from petroleum. However, the targeted upgrading of lignocellulosic biomass typically involves an initial chemical process to produce platform molecules that serve as the basis for further upgrading processes, including: (i) sugars, (ii) dehydration products, (iii) polyols and (iv) lignin monomers. All of these platform molecules can be produced from lignocellulosic biomass in a single stage. The viability of this initial processing step can have a strong effect on the economics and sustainability of the overall process for conversion of biomass to fuels and chemicals. Accordingly, we have systematically reported the important factors affecting process economics and sustainability including product yield, catalyst usage, processing conditions and product concentrations. In this respect, not all biomass-derived molecules are equal. Sugars can be produced at high concentrations (>10 wt%) using monophasic processes and simple catalysts (usually a mineral acid). In contrast, furans (furfural and HMF) are difficult to produce simultaneously at high concentrations and high yields due to condensation reactions leading to solid degradation products (resinification). The high reactivity of these molecules leads to the use of more complex reaction systems—such as biphasic mixtures, continuous product distillation and ionic liquids—or the use of homogeneous Lewis acids. These considerations also apply to the production of levulinic acid, because although it is stable at typical reaction conditions, it is dependent on the formation of intermediate furanic species. Finally, initial efforts to convert lignin have led to lower yields (<50%) and have only rarely been integrated with the upgrading of the other biomass fractions.

In this review, we have focused on studies and technologies that have reported yields for real biomass, as opposed to studies of model compounds (*e.g.*, cellulose, glucose, xylose). Mineral acid catalysts typically behave in a similar fashion with real biomass and model compounds, even though the quantities of acid used have to be adjusted to compensate for the neutralization capacity of the specific biomass feedstock. In contrast, solid catalysts may undergo deactivation when real lignocellulosic biomass is used as a feedstock. Ionic liquids appear to be robust solvents, as illustrated by their ability to operate with high biomass concentrations, especially in the case of HMF production. However, because of their cost, even a small loss of activity or limited consumption by biomass

could significantly limit the economics of the overall process. A similar remark can be made regarding the uses of solvents in general in biomass conversion processes.

The examples presented in this review illustrate the need for future research to more systematically address the factors that control the conversion of real lignocellulosic biomass. The use of model compounds is an essential tool to identify reaction pathways and to discover new catalysts; however, it is crucial to study the effects of using real biomass on catalyst activity and selectivity. It is especially important to address the impact of real biomass on the recovery, recycling, and potential regeneration of catalysts and solvents used in the biomass conversion processes. It is also essential to integrate the upgrading of all three biomass fractions. Such considerations are important if the production of fuels and/or commodity chemicals from biomass is to be employed as an alternative to the highly optimized and efficient production of these commodity products made from crude oil.

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## Notes and references

- 1 J. W. Tester, *Sustainable energy*, MIT Press, 2005.
- 2 J. Houghton, *Breaking the biological barriers to cellulosic ethanol: A joint research agenda*, US Department of Energy, Rockville, Maryland, 2005.
- 3 S. K. Lee, H. Chou, T. S. Ham, T. S. Lee and J. D. Keasling, *Curr. Opin. Biotechnol.*, 2008, **19**, 556–563.
- 4 J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, 2010, **327**, 1110–1114.
- 5 G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446–1450.
- 6 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
- 7 H. Lieth, *Primary Productivity of the Biosphere*, Springer Verlag, New York, 1975.
- 8 D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.
- 9 A. H. Zacher, M. V. Olarte, D. M. Santosa, D. C. Elliott and S. B. Jones, *Green Chem.*, 2014, **16**, 491–515.
- 10 A. V. Bridgwater, *Biomass Bioenergy*, 2012, **38**, 68–94.
- 11 D. A. Bulushev and J. R. H. Ross, *Catal. Today*, 2011, **171**, 1–13.
- 12 H. de Lasa, E. Salices, J. Mazumder and R. Lucky, *Chem. Rev.*, 2011, **111**, 5404–5433.

- 13 B. Digman, H. S. Joo and D.-S. Kim, *Environ. Prog. Sustainable Energy*, 2009, **28**, 47–51.
- 14 D. C. Elliott, *Biofuels, Bioprod. Biorefin.*, 2008, **2**, 254–265.
- 15 J. Lédé, *Oil Gas Sci. Technol. – Rev. D'IFP Energ. Nouv.*, 2013, **68**, 801–814.
- 16 A. A. Peterson, F. Vogel, R. P. Lachance, M. Fröling, J. Michael, J. Antal and J. W. Tester, *Energy Environ. Sci.*, 2008, **1**, 32–65.
- 17 S. S. Toor, L. Rosendahl and A. Rudolf, *Energy*, 2011, **36**, 2328–2342.
- 18 G. Brodeur, E. Yau, K. Badal, J. Collier, K. B. Ramachandran and S. Ramakrishnan, *Enzyme Res.*, 2011, **2011**, 1–17.
- 19 H. Tadesse and R. Luque, *Energy Environ. Sci.*, 2011, **4**, 3913–3929.
- 20 Y. Zheng, Z. Pan and R. Zhang, *Int. J. Agric. Biol. Eng.*, 2009, **2**, 51–68.
- 21 C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, Y. Y. Lee, C. Mitchinson and J. N. Saddler, *Biotechnol. Prog.*, 2009, **25**, 333–339.
- 22 C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch and Y. Y. Lee, *Bioresour. Technol.*, 2005, **96**, 2026–2032.
- 23 P. Alvira, E. Tomás-Pejó, M. Ballesteros and M. J. Negro, *Bioresour. Technol.*, 2010, **101**, 4851–4861.
- 24 F. M. Gírio, C. Fonseca, F. Carvalheiro, L. C. Duarte, S. Marques and R. Bogel-Lukasik, *Bioresour. Technol.*, 2010, **101**, 4775–4800.
- 25 A. A. Modenbach and S. E. Nokes, *Biomass Bioenergy*, 2013, **56**, 526–544.
- 26 M. Galbe and G. Zacchi, *Biomass Bioenergy*, 2012, **46**, 70–78.
- 27 A. Brandt, J. Gräsvik, J. P. Hallett and T. Welton, *Green Chem.*, 2013, **15**, 550–583.
- 28 A. M. da C. Lopes, K. G. João, A. R. C. Morais, E. Bogel-Lukasik and R. Bogel-Lukasik, *Sustainable Chem. Processes*, 2013, **1**, 3.
- 29 D. Klein-Marcuschamer, P. Oleskowicz-Popiel, B. A. Simmons and H. W. Blanch, *Biotechnol. Bioeng.*, 2012, **109**, 1083–1087.
- 30 H. Braconnot, *Ann. Chim. Phys.*, 1819, **12**, 172–195.
- 31 A. L. Stern, *J. Chem. Soc. Trans.*, 1895, **67**, 74–90.
- 32 F. Bergius, *Ind. Eng. Chem.*, 1937, **29**, 247–253.
- 33 E. Baniel, *Refined Cellulosic Sugars and Lignin-Opportunities Louisiana Shouldn't miss, Louisiana Biofuels and Bioprocessing Summit*, Louisiana, 2012.
- 34 A. Baniel and A. Eyal, *US Patent No US20100093995*, 2010.
- 35 A. M. Baniel, *US Patent No US4291007*, 1981.
- 36 A. Eyal and A. Baniel, *Ind. Eng. Chem. Process Des. Dev.*, 1982, **21**, 334–337.
- 37 A. Eyal, R. Jansen, A. Vitner and R. Mali, *European Patent No EP2585606*, 2013.
- 38 A. Eyal and R. Jansen, *US Patent No US20120227733*, 2012.
- 39 R. Erckel, R. Franz, T. Riehm and R. Woernle, *US Patent No US4556431*, 1985.
- 40 S. M. Selke, M. C. Hawley, H. Hardt, D. T. A. Lamport, G. Smith and J. Smith, *Ind. Eng. Chem. Prod. Res. Dev.*, 1982, **21**, 11–16.
- 41 A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, *Determination of structural carbohydrates and lignin in biomass*, National Renewable Energy Laboratory, Golden, CO, 2004.
- 42 M. A. Harmer, A. Fan, A. Liauw and R. K. Kumar, *Chem. Commun.*, 2009, 6610.
- 43 N. Meine, R. Rinaldi and F. Schüth, *ChemSusChem*, 2012, **5**, 1449–1454.
- 44 S. M. Hick, C. Griebel, D. T. Restrepo, J. H. Truitt, E. J. Buker, C. Bylda and R. G. Blair, *Green Chem.*, 2010, **12**, 468–474.
- 45 Q. Zhang and F. Jérôme, *ChemSusChem*, 2013, **6**, 2042–2044.
- 46 M. Kaldström, N. Meine, C. Farès, R. Rinaldi and F. Schüth, *Green Chem.*, 2014, **16**, 2454–2462.
- 47 O. Bobleter, *Prog. Polym. Sci.*, 1994, **19**, 797–841.
- 48 S. K. R. Patil and C. R. F. Lund, *Energy Fuels*, 2011, **25**, 4745–4755.
- 49 A. Esteghlalian, A. G. Hashimoto, J. J. Fenske and M. H. Penner, *Bioresour. Technol.*, 1997, **59**, 129–136.
- 50 R. D. Fagan, H. E. Grethlein, A. O. Converse and A. Porteous, *Environ. Sci. Technol.*, 1971, **5**, 545–547.
- 51 J. F. Saeman, *Ind. Eng. Chem.*, 1945, **37**, 43–52.
- 52 J. F. Harris, A. J. Baker, A. Conner, T. Jeffries, J. Minor, R. Pettersen, R. Scott, E. Springer, T. Wegner and J. Zerbe, *Gen. Tech. Rep. FPL*, 1985, 45.
- 53 Y. Y. Lee, P. Iyer and R. W. Torget, in *Recent Progress in Bioconversion of Lignocellulosics*, ed. P. D. G. T. Tsao, A. P. Brainard, H. R. Bungay, N. J. Cao, P. Cen, Z. Chen, J. Du, B. Foody, C. S. Gong, P. Hall, N. W. Y. Ho, D. C. Irwin, P. Iyer, T. W. Jeffries, C. M. Ladisch, M. R. Ladisch, Y. Y. Lee, N. S. Mosier, H. M. Mühlemann, M. Sedlak, N.-Q. Shi, G. T. Tsao, J. S. Tolan, R. W. Torget, D. B. Wilson and L. Xia, Springer, Berlin, Heidelberg, 1999, pp. 93–115.
- 54 W. L. Faith, *Ind. Eng. Chem.*, 1945, **37**, 9–11.
- 55 E. E. Harris and E. Beglinger, *Ind. Eng. Chem.*, 1946, **38**, 890–895.
- 56 N. Gilbert, I. A. Hobbs and J. D. Levine, *Ind. Eng. Chem.*, 1952, **44**, 1712–1720.
- 57 R. Chen, Z. Wu and Y. Y. Lee, *Appl. Biochem. Biotechnol.*, 1998, **70–72**, 37–49.
- 58 S. K. Song and Y. Y. Lee, *Chem. Eng. Commun.*, 1982, **17**, 23–30.
- 59 A. V. Bandura and S. N. Lvov, *J. Phys. Chem. Ref. Data*, 2006, **35**, 15–30.
- 60 Y. Zhao, W.-J. Lu, H.-T. Wang and J.-L. Yang, *Bioresour. Technol.*, 2009, **100**, 5884–5889.
- 61 M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri and K. Arai, *Ind. Eng. Chem. Res.*, 2000, **39**, 2883–2890.
- 62 D. A. Cantero, M. Dolores Bermejo and M. José Cocero, *Bioresour. Technol.*, 2013, **135**, 697–703.
- 63 D. A. Cantero, M. D. Bermejo and M. J. Cocero, *J. Supercrit. Fluids*, 2013, **75**, 48–57.

- 64 M. Hamilton, *Low cost cellulosic sugar: the ultimate feedstock*, World Congress on Industrial Biotechnology & Bioprocessing, Toronto, Canada, 2011.
- 65 S. Kilambi and K. L. Kadam, *US Patent No US20130239954*, 2013.
- 66 S. Kilambi, K. Kadam and C. A. Martin, *US Patent No US8568533*, 2013.
- 67 Y. Kim, N. S. Mosier and M. R. Ladisch, *Biotechnol. Prog.*, 2009, **25**, 340–348.
- 68 N. S. Mosier, R. Hendrickson, M. Brewer, N. Ho, M. Sedlak, R. Dreshel, G. Welch, B. S. Dien, A. Aden and M. R. Ladisch, *Appl. Biochem. Biotechnol.*, 2005, **125**, 77–97.
- 69 G. Garrote, H. Dominguez and J. C. Parajo, *J. Chem. Technol. Biotechnol.*, 1999, **74**, 1101–1109.
- 70 I. A. Ares-Peón, C. Vila, G. Garrote and J. C. Parajo, *J. Chem. Technol. Biotechnol.*, 2011, **86**, 251–260.
- 71 D. C. Floyd, K. Kadam and S. Kilambi, *US Patent No US20130172546*, 2013.
- 72 P. R. Gibbs, *US Patent No US20120282656*, 2012.
- 73 K. H. Kim and J. Hong, *Bioresour. Technol.*, 2001, **77**, 139–144.
- 74 J. S. Luterbacher, J. W. Tester and L. P. Walker, *Biotechnol. Bioeng.*, 2010, **107**, 451–460.
- 75 J. S. Luterbacher, J. W. Tester and L. P. Walker, *Biotechnol. Bioeng.*, 2012, **109**, 1499–1507.
- 76 J. S. Luterbacher, Q. Chew, Y. Li, J. W. Tester and L. P. Walker, *Energy Environ. Sci.*, 2012, **5**, 6990–7000.
- 77 S. P. M. da Silva, A. R. C. Morais and R. Bogel-Lukasik, *Green Chem.*, 2013, **16**, 238–246.
- 78 J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger and J. A. Dumesic, *Science*, 2014, **343**, 277–280.
- 79 D. M. Alonso, S. G. Wettstein, M. A. Mellmer, E. I. Gurbuz and J. A. Dumesic, *Energy Environ. Sci.*, 2013, **6**, 76–80.
- 80 M. A. Mellmer, C. Sener, J. M. R. Gallo, J. S. Luterbacher, D. M. Alonso and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2014, **53**, 11872–11875.
- 81 M. A. Mellmer, D. M. Alonso, J. S. Luterbacher, J. M. R. Gallo and J. A. Dumesic, *Green Chem.*, 2014, **16**, 4659–4662.
- 82 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974–4975.
- 83 J. B. Binder and R. T. Raines, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 4516–4521.
- 84 C. Sievers, M. B. Valenzuela-Olarte, T. Marzalletti, I. Musin, P. K. Agrawal and C. W. Jones, *Ind. Eng. Chem. Res.*, 2009, **48**, 1277–1286.
- 85 L. Vanoye, M. Fanselow, J. D. Holbrey, M. P. Atkins and K. R. Seddon, *Green Chem.*, 2009, **11**, 390–396.
- 86 A. S. Amarasekara and O. S. Owereh, *Ind. Eng. Chem. Res.*, 2009, **48**, 10152–10155.
- 87 R. Rinaldi, R. Palkovits and F. Schüth, *Angew. Chem., Int. Ed.*, 2008, **47**, 8047–8050.
- 88 H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597–1600.
- 89 N. Sun, H. Liu, N. Sathitsuksanoh, V. Stavila, M. Sawant, A. Bonito, K. Tran, A. George, K. L. Sale, S. Singh, B. A. Simmons and B. M. Holmes, *Biotechnol. Biofuels*, 2013, **6**, 1–15.
- 90 K. J. Zeitsch, *The Chemistry and Technology of Furfural and its Many By-Products*, Elsevier, 2000.
- 91 K. J. Zeitsch, *US Patent No US4912237*, 1990.
- 92 K. J. Zeitsch, *US Patent No US6743928*, 2004.
- 93 W. De Jong and G. Marcotullio, *Int. J. Chem. React. Eng.*, 2010, **8**, 1542–6580.
- 94 K. Triantafyllidis, A. Lappas and M. Stöcker, *The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals*, Newnes, 2013.
- 95 G. Marcotullio, *The Chemistry and Technology of Furfural Production in Modern Lignocellulose-feedstock Biorefineries*, Arkh , 2011.
- 96 D.-C. Bo and P.-L. Li, *Chem. Ind. For. Prod.*, 2013, **33**, 128–134.
- 97 B. Danon, G. Marcotullio and W. De Jong, *Green Chem.*, 2014, **16**, 39–54.
- 98 X. Guo, Y. Yan, Y. Zhang and Y. Tang, *Prog. Chem.*, 2013, **25**, 1915–1927.
- 99 J.-P. Lange, E. van der Heide, J. van Buijtenen and R. Price, *ChemSusChem*, 2012, **5**, 150–166.
- 100 S. Dutta, S. De, B. Saha and M. I. Alam, *Catal. Sci. Technol.*, 2012, **2**, 2025–2036.
- 101 R. Karinen, K. Vilonen and M. Niemel , *ChemSusChem*, 2011, **4**, 1002–1016.
- 102 F. Jin and H. Enomoto, *Energy Environ. Sci.*, 2011, **4**, 382–397.
- 103 E. I. G rb z, J. M. R. Gallo, D. M. Alonso, S. G. Wettstein, W. Y. Lim and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2013, **52**, 1270–1274.
- 104 R. L. Whistler, H. E. Conrad and L. Hough, *J. Am. Chem. Soc.*, 1954, **76**, 1668–1670.
- 105 J. M. R. Gallo, D. M. Alonso, M. A. Mellmer, J. H. Yeap, H. C. Wong and J. A. Dumesic, *Top. Catal.*, 2013, **56**, 1775–1781.
- 106 C. D. Hurd and L. L. Isenhour, *J. Am. Chem. Soc.*, 1932, **54**, 317–330.
- 107 O. Yemiř and G. Mazza, *Bioresour. Technol.*, 2011, **102**, 7371–7378.
- 108 Y. Roman-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933.
- 109 Y. Roman-Leshkov and J. A. Dumesic, *Top. Catal.*, 2009, **52**, 297–303.
- 110 A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani, *Chem. Lett.*, 2010, **39**, 838–840.
- 111 V. Choudhary, A. B. Pinar, S. I. Sandler, D. G. Vlachos and R. F. Lobo, *ACS Catal.*, 2011, **1**, 1724–1728.
- 112 V. Choudhary, S. I. Sandler and D. G. Vlachos, *ACS Catal.*, 2012, **2**, 2022–2028.
- 113 M. J. Campos Molina, R. Mariscal, M. Ojeda and M. L pez Granados, *Bioresour. Technol.*, 2012, **126**, 321–327.
- 114 G. Marcotullio and W. De Jong, *Green Chem.*, 2010, **12**, 1739–1746.

- 115 H. Amiri, K. Karimi and S. Roodpeyma, *Carbohydr. Res.*, 2010, **345**, 2133–2138.
- 116 Y. Roman-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.
- 117 Y. Yang, C.-W. Hu and M. M. Abu-Omar, *ChemSusChem*, 2012, **5**, 405–410.
- 118 E. I. Gürbüz, S. G. Wettstein and J. A. Dumesic, *ChemSusChem*, 2012, **5**, 383–387.
- 119 D. M. Alonso, S. G. Wettstein, M. A. Mellmer, E. I. Gurbuz and J. A. Dumesic, *Energy Environ. Sci.*, 2012, **6**, 76–80.
- 120 L. Zhang, H. Yu, P. Wang and Y. Li, *Bioresour. Technol.*, 2014, **151**, 355–360.
- 121 C. M. Cai, T. Zhang, R. Kumar and C. E. Wyman, *Green Chem.*, 2013, **15**, 3140–3145.
- 122 L. Zhang, H. Yu and P. Wang, *Bioresour. Technol.*, 2013, **136**, 515–521.
- 123 J. van Buijtenen, J.-P. Lange, L. E. Alonso, W. Spiering, R. F. Polmans and R. J. Haan, *ChemSusChem*, 2013, **6**, 2132–2136.
- 124 E. S. Kim, S. Liu, M. M. Abu-Omar and N. S. Mosier, *Energy Fuels*, 2012, **26**, 1298–1304.
- 125 K.-H. Lin, M.-H. Huang and A. C.-C. Chang, *Int. J. Hydrogen Energy*, 2013, **38**, 15794–15800.
- 126 C. Rong, X. Ding, Y. Zhu, Y. Li, L. Wang, Y. Qu, X. Ma and Z. Wang, *Carbohydr. Res.*, 2012, **350**, 77–80.
- 127 R. Weingarten, J. Cho, R. Xing, W. C. Conner and G. W. Huber, *ChemSusChem*, 2012, **5**, 1280–1290.
- 128 J. Shen and C. E. Wyman, *AIChE J.*, 2012, **58**, 236–246.
- 129 B. Girisuta, L. P. B. M. Janssen and H. J. Heeres, *Ind. Eng. Chem. Res.*, 2007, **46**, 1696–1708.
- 130 B. Girisuta, L. Janssen and H. J. Heeres, *Chem. Eng. Res. Des.*, 2006, **84**, 339–349.
- 131 C. Chang, P. Cen and X. Ma, *Bioresour. Technol.*, 2007, **98**, 1448–1453.
- 132 <http://biofinetechnology.com/>.
- 133 D. J. Hayes, S. Fitzpatrick, M. H. B. Hayes and J. R. H. Ross, in *Biorefineries-Industrial Processes and Products*, ed. B. Kamm, P. R. Gruber and M. Kamm, Wiley-VCH Verlag GmbH, 2008, pp. 139–164.
- 134 S. W. Fitzpatrick, *US Patent* No US5608105, 1997.
- 135 S. W. Fitzpatrick, *US Patent* No US4897497, 1990.
- 136 B. Girisuta, K. Dussan, D. Haverty, J. J. Leahy and M. H. B. Hayes, *Chem. Eng. J.*, 2013, **217**, 61–70.
- 137 A. M. R. Galletti, C. Antonetti, V. De Luise, D. Licursi and N. N. O. Di Nasso, *Bioresources*, 2012, **7**, 1824–1835.
- 138 A. M. R. Galletti, C. Antonetti, E. Ribechini, M. P. Colombini, N. N. O. Di Nasso and E. Bonari, *Appl. Energy*, 2013, **102**, 157–162.
- 139 J. Potvin, E. Sorlien, J. Hegner, B. DeBoef and B. L. Lucht, *Tetrahedron Lett.*, 2011, **52**, 5891–5893.
- 140 S. M. Sen, D. M. Alonso, S. G. Wettstein, E. I. Guerbuez, C. A. Henao, J. A. Dumesic and C. T. Maravelias, *Energy Environ. Sci.*, 2012, **5**, 9690–9697.
- 141 D. J. Braden, C. A. Henao, J. Heltzel, C. T. Maravelias and J. A. Dumesic, *Green Chem.*, 2011, **13**, 1755–1765.
- 142 H. Chen, B. Yu and S. Jin, *Bioresour. Technol.*, 2011, **102**, 3568–3570.
- 143 S. Li and E. W. Qian, *J. Jpn. Inst. Energy*, 2011, **90**, 1065–1071.
- 144 D. M. Alonso, S. G. Wettstein, J. Q. Bond, T. W. Root and J. A. Dumesic, *ChemSusChem*, 2011, **4**, 1078–1081.
- 145 K. Dussan, B. Girisuta, D. Haverty, J. J. Leahy and M. H. B. Hayes, *Bioresour. Technol.*, 2013, **149**, 216–224.
- 146 D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Green Chem.*, 2013, **15**, 584.
- 147 S. G. Wettstein, D. M. Alonso, Y. Chong and J. A. Dumesic, *Energy Environ. Sci.*, 2012, **5**, 8199.
- 148 M. E. Zakrzewska, E. Bogel-Lukasik and R. Bogel-Lukasik, *Chem. Rev.*, 2011, **111**, 397–417.
- 149 J. B. Binder and R. T. Raines, *J. Am. Chem. Soc.*, 2009, **131**, 1979–1985.
- 150 Y. Yang, C. Hu and M. M. Abu-Omar, *Green Chem.*, 2012, **14**, 509.
- 151 R. Carrasquillo-Flores, M. Källdström, F. Schüth, J. A. Dumesic and R. Rinaldi, *ACS Catal.*, 2013, **3**, 993–997.
- 152 S. Dutta, S. De, M. I. Alam, M. M. Abu-Omar and B. Saha, *J. Catal.*, 2012, **288**, 8–15.
- 153 M. Mascal and E. B. Nikitin, *Angew. Chem.*, 2008, **120**, 8042–8044.
- 154 M. Mascal and E. B. Nikitin, *Green Chem.*, 2010, **12**, 370.
- 155 M. Mascal and E. B. Nikitin, *ChemSusChem*, 2009, **2**, 423–426.
- 156 E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gartner and J. A. Dumesic, *Science*, 2008, **322**, 417.
- 157 R. D. Cortright, R. R. Davda and J. Dumesic, *Nature*, 2002, **418**, 964–967.
- 158 N. Li, G. A. Tompsett, T. Zhang, J. Shi, C. E. Wyman and G. W. Huber, *Green Chem.*, 2011, **13**, 91–101.
- 159 R. Palkovits, K. Tajvidi, J. Procelewska, R. Rinaldi and A. Ruppert, *Green Chem.*, 2010, **12**, 972–978.
- 160 J. Hilgert, N. Meine, R. Rinaldi and F. Schüth, *Energy Environ. Sci.*, 2012, **6**, 92–96.
- 161 I. A. Ignatyev, C. Van Doorslaer, P. G. N. Mertens, K. Binnemans and D. E. De Vos, *ChemSusChem*, 2010, **3**, 91–96.
- 162 W. Zhu, H. Yang, J. Chen, C. Chen, L. Guo, H. Gan, X. Zhao and Z. Hou, *Green Chem.*, 2014, **16**, 1534–1542.
- 163 G. Yi and Y. Zhang, *ChemSusChem*, 2012, **5**, 1383–1387.
- 164 J. Michael Robinson, C. E. Burgess, M. A. Bently, C. D. Brasher, B. O. Horne, D. M. Lillard, J. M. Macias, H. D. Mandal, S. C. Mills, K. D. O'Hara, J. T. Pon, A. F. Raigoza, E. H. Sanchez and J. S. Villarreal, *Biomass Bioenergy*, 2004, **26**, 473–483.
- 165 J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.
- 166 J. R. Bower, L. M. Cooke and H. Hibbert, *J. Am. Chem. Soc.*, 1943, **65**, 1192–1195.
- 167 C. P. Brewer, L. M. Cooke and H. Hibbert, *J. Am. Chem. Soc.*, 1948, **70**, 57–59.

- 168 J. M. Pepper and Y. W. Lee, *Can. J. Chem.*, 1969, **47**, 723–727.
- 169 P. Azadi, R. Carrasquillo-Flores, Y. J. Pagán-Torres, E. I. Gürbüz, R. Farnood and J. A. Dumesic, *Green Chem.*, 2012, **14**, 1573–1576.
- 170 N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. Liu and Y. Kou, *ChemSusChem*, 2008, **1**, 626–629.
- 171 C. Li, M. Zheng, A. Wang and T. Zhang, *Energy Environ. Sci.*, 2012, **5**, 6383–6390.
- 172 M. P. Pandey and C. S. Kim, *Chem. Eng. Technol.*, 2011, **34**, 29–41.
- 173 J. M. Genco, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 2000.
- 174 T. Voith and P. R. von Rohr, *ChemSusChem*, 2008, **1**, 763–769.
- 175 J. Zakzeski, A. L. Jongerijs, P. C. A. Bruijninx and B. M. Weckhuysen, *ChemSusChem*, 2012, **5**, 1602–1609.
- 176 T. Voith and P. R. Rohr, *Ind. Eng. Chem. Res.*, 2010, **49**, 520–525.
- 177 H. Werhan, J. M. Mir, T. Voith and von R. P. Rudolf, *Holzforschung*, 2011, **65**, 703–709.
- 178 J. D. P. Araújo, C. A. Grande and A. E. Rodrigues, *Chem. Eng. Res. Des.*, 2010, **88**, 1024–1032.
- 179 H.-R. Bjørsvik and F. Minisci, *Org. Process Res. Dev.*, 1999, **3**, 330–340.
- 180 V. M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li and J. A. Lercher, *Chem. – Eur. J.*, 2011, **17**, 5939–5948.
- 181 J. S. Shabtai, W. W. Zmierzak and E. Chornet, *US patent* No US5959167, 1999.
- 182 A. J. Ragauskas, G. T. Beckham, M. J. Bidy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan and C. E. Wyman, *Science*, 2014, **344**, 1246843.
- 183 A. Eyal, A. Vitner and R. Mali, *European Union Patent* No EP2531275 A1, 2012.
- 184 D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof and M. Worley, *Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol*, *National Renewable Energy Laboratory Report*, TP-5100-47764, 2011.
- 185 S. Haley, *USDA Economic Research Service - SSSM306*, USDA, 2014.
- 186 S. M. Sen, J. B. Binder, R. T. Raines and C. T. Maravelias, *Biofuels, Bioprod. Biorefin.*, 2012, **6**, 444–452.
- 187 L. Chen, M. Sharifzadeh, N. Mac Dowell, T. Welton, N. Shah and J. P. Hallett, *Green Chem.*, 2014, **16**, 3098.
- 188 J. Han, S. M. Sen, D. M. Alonso, J. A. Dumesic and C. T. Maravelias, *Green Chem.*, 2014, **16**, 653–661.
- 189 A. Wingren, M. Galbe and G. Zacchi, *Biotechnol. Prog.*, 2003, **19**, 1109–1117.
- 190 Z. Fan, C. South, K. Lyford, J. Munsie, P. van Walsum and L. Lynd, *Bioprocess Biosyst. Eng.*, 2003, **26**, 93–101.
- 191 H. Jorgensen, J. Vibe-Pedersen, J. Larsen and C. Felby, *Biotechnol. Bioeng.*, 2007, **96**, 862–870.
- 192 D. Humbird and A. Aden, *Biochemical production of ethanol from corn stover: 2008 state of technology model*, National Renewable Energy Laboratory, 2009.
- 193 D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Green Chem.*, 2013, **15**, 584–595.
- 194 A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754–793.
- 195 Global Sorbitol Market is Expected to Reach USD 3 Billion in 2018: Transparency Market Research, *PRNewswire*, February 18<sup>th</sup> 2013.
- 196 F. Zaworski, US 2011 sorbitol contracts jump 15%, tracking higher corn prices, *ICIS News*, January 4<sup>th</sup> 2011.
- 197 J. C. Serrano-Ruiz, R. Luque and A. Sepúlveda-Escribano, *Chem. Soc. Rev.*, 2011, **40**, 5266.
- 198 S. Pedersen, *Chemicals from sugars*, *Topsoe catalysis forum*, Denmark, Sept 17<sup>th</sup> 2008.
- 199 W. Schwald and O. Bobleter, *J. Carbohydr. Chem.*, 1989, **8**, 565–578.
- 200 T. Adschiri, S. Hirose, R. Malaluan and K. Arai, *J. Chem. Eng. Jpn.*, 1993, **26**, 676–680.
- 201 K. Mochidzuki, A. Sakoda and M. Suzuki, *Thermochim. Acta*, 2000, **348**, 69–76.
- 202 O. Bobleter and G. Pape, *Monatsh. Chem.*, 1968, **99**, 1560.
- 203 S. Amin, R. C. Reid and M. Modell, in *ASME, SAE, AIAA, ASMA, and AIChE, Intersociety Conference on Environmental Systems*, San Francisco, Calif, 1975.
- 204 B. M. Kabyemela, T. Adschiri, R. M. Malaluan and K. Arai, *Ind. Eng. Chem. Res.*, 1997, **36**, 1552–1558.
- 205 Y. Matsumura, S. Yanachi and T. Yoshida, *Ind. Eng. Chem. Res.*, 2006, **45**, 1875–1879.
- 206 R. A. Antonoplis, H. W. Blanch, R. P. Freitas, A. F. Sciamanna and C. R. Wilke, *Biotechnol. Bioeng.*, 1983, **25**, 2757–2773.
- 207 A. Eyal, R. Jansen, A. Vitner and R. Mali, *European Union Patent* No EP2585823, 2013.
- 208 M. Mascal and E. B. Nikitin, *ChemSusChem*, 2009, **2**, 423–426.
- 209 S. W. Fitzpatrick, *US patent* No US4897497, 1990.
- 210 D. Klein-Marcuschamer, B. A. Simmons and H. W. Blanch, *Biofuels, Bioprod. Biorefin.*, 2011, **5**, 562–569.
- 211 F. K. Kazi, A. D. Patel, J. C. Serrano-Ruiz, J. A. Dumesic and R. P. Anex, *Chem. Eng. J.*, 2011, **169**, 329–338.
- 212 F. Zaworski, *OUTLOOK '13: Sorbitol prices to rise 8% in 2013*, *ICIS News*, January 7<sup>th</sup> 2013.