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# The conversion of lignocellulosics to levulinic acid

Darryn W Rackemann and William OS Doherty, Centre for Tropical Crops and Biocommodities, Queensland University of Technology, Brisbane 4001, Australia

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**Abstract:** Biomass represents an abundant and relatively low cost carbon resource that can be utilized to produce platform chemicals such as levulinic acid. Current processing technology limits the cost-effective production of levulinic acid in commercial quantities from biomass. The key to improving the yield and efficiency of levulinic acid production from biomass lies in the ability to optimize and isolate the intermediate products at each step of the reaction pathway and reduce re-polymerization and side reactions. New technologies (including the use of microwave irradiation and ionic liquids) and the development of highly selective catalysts would provide the necessary step change for the optimization of key reactions. A processing environment that allows the use of biphasic systems and/or continuous extraction of products would increase reaction rates, yields and product quality. This review outlines the chemistry of levulinic acid synthesis and discusses current and potential technologies for producing levulinic acid from lignocellulosics. © 2011 Society of Chemical Industry and John Wiley & Sons, Ltd

**Keywords:** lignocellulosics; hydrolysis; levulinic acid; hydroxymethylfurfural

## Introduction

The bulk of energy needs and vast majority of synthetic products and chemicals have historically been sourced from fossil fuels due to their abundant supply and relatively low cost. Eventually the utilization of fossil resources will become unsustainable due to world population increases and modernisation, rising prices and decline of available fossil resources and environmental pressures (due to toxic emissions).<sup>1</sup> In contrast to other renewable energy resources (solar, thermal, tidal, wind, hydro etc), biomass is the only renewable resource of fixed carbon, which is essential for the production of liquid hydrocarbon fuels and chemicals.<sup>2-5</sup>

Nature produces over 150 billion tonnes of biomass per year by photosynthesis, with only 3–4% used by humans for food and non-food purposes.<sup>5</sup> Low value agricultural and forestry residues, grasses and energy crops are the preferred sources of biomass from both a techno- and socio-economic point of view, as the biomass feedstock does not compete with the food chain.<sup>6,7</sup> A substantial amount of research is currently being carried out worldwide to identify attractive chemical transformations of biomass into bulk organic chemicals.<sup>7</sup>

National Renewable Energy Laboratory (Denver, USA) identified levulinic acid as one of a number of key

Correspondence to: Darryn W Rackemann, Centre for Tropical Crops and Biocommodities, Queensland University of Technology, 2 George Street, Brisbane 4001, Australia. Email: d.rackemann@qut.edu.au;

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sugar-derived platform chemicals that can be produced from biomass.<sup>8,9</sup> Levulinic acid, a member of the gamma-keto acids, can be produced through acid-catalyzed dehydration and hydrolysis of hexose sugars. It is an ideal platform chemical that can be utilized to produce a number of bio-chemicals including succinic acid, resins, polymers, herbicides, pharmaceuticals and flavouring agents, solvents, plasticisers, anti-freeze agents and biofuels/oxygenated fuel additives as shown in Figure 1.<sup>10–12</sup> Some of the biofuel derivatives of levulinic acid such as 2-methyl-tetrahydrofuran and  $\gamma$ -valerolactone can be readily blended with petroleum products to create cleaner-burning fuels with the advantage that they do not suffer from phase separation to become contaminated with water (*c.f.* ethanol). Alternatively  $\gamma$ -valerolactone can be converted to valeric biofuels by esterification to pentenoate esters<sup>13</sup> or hydrogenated to pentanoic acid which can be catalytically upgraded to 5-nonanone by ketonization and hydrogenated to alkanes or alcohols (depending on the catalyst employed). The alcohols can be subsequently dehydrated to alkenes and oligomerized enabling the production of C<sub>6</sub>-C<sub>27</sub> hydrocarbon fuels.<sup>14–16</sup> A recently developed thermal de-oxygenation process is also able to convert levulinic acid to energy dense (low

oxygen to carbon ratio) cyclic and aromatic products that may be easily upgraded to hydrocarbon fuels.<sup>17</sup>

The major intermediate in the dehydration/hydrolysis process of levulinic acid from hexose sugars is 5-hydroxymethylfurfural (HMF). While HMF is unstable under acidic conditions, it can be catalytically converted to energy dense biofuels such as 2-methylfuran and 2,5-dimethylfuran in aqueous solvents<sup>18–20</sup> or oxidised to highly functional monomers such as 2,5-furandicarbaldehyde and 2,5-furandicarboxylic acid (FDCA).<sup>21,22</sup> FDCA is a monomer for production of many polymers and has been touted as a green replacement for terephthalic acid and polyethylene terephthalate, principally used as a precursor to polyester for clothing and plastic bottles.<sup>21</sup>

In the acid-catalyzed conversion of hexose sugars to levulinic acid, formic acid is co-produced. Formic acid is a low value commodity chemical used in the production of formaldehyde, rubber, plasticizers, pharmaceuticals and textiles but in future may find increased utilization in fuel cell applications,<sup>23</sup> as a feed source for hydrogen storage and production,<sup>24</sup> or used in the transfer hydrogenation of levulinic acid to higher value products.<sup>15,25–27</sup>

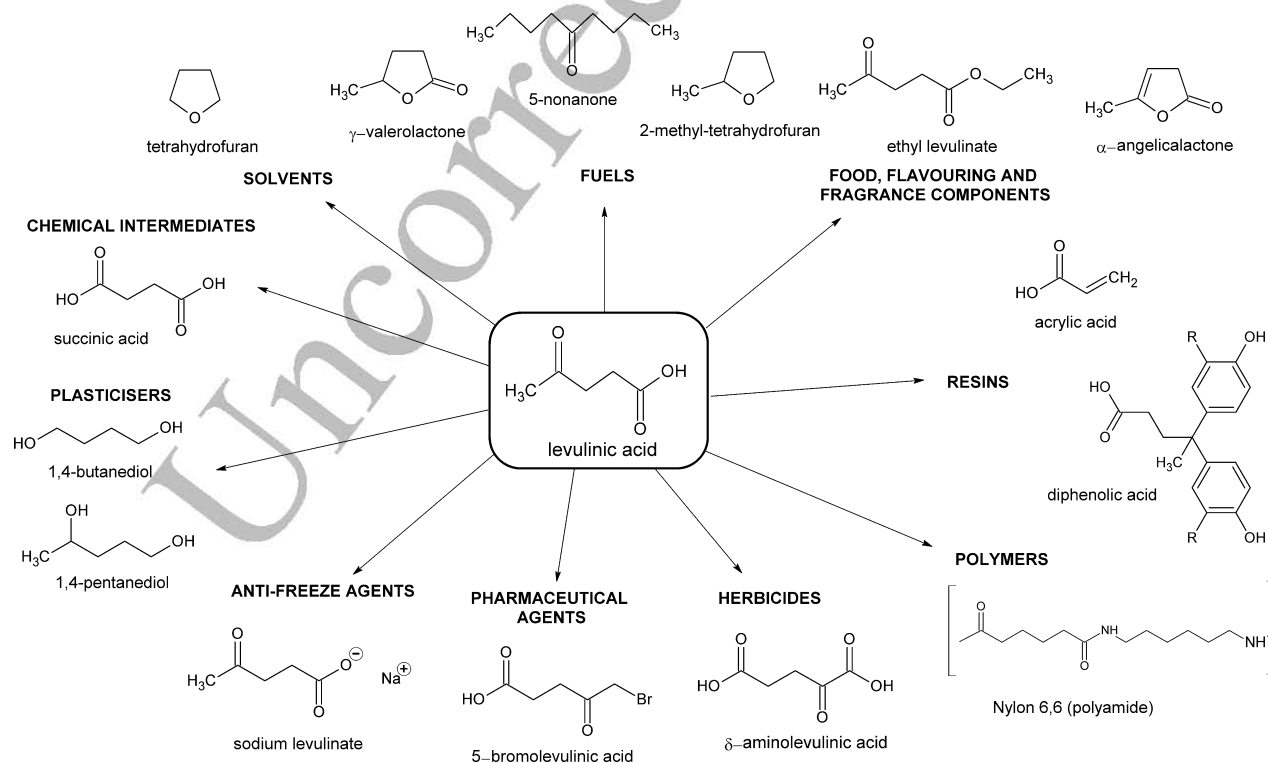


Figure 1. Levulinic acid as a platform chemical for other chemical products and fuels.

One of the reasons why levulinic acid has not been produced in commercial quantities is the cost of the raw materials used for its synthesis. The main method for production of high purity levulinic acid in use today involves the petrochemical conversion route from maleic anhydride<sup>28</sup> or hydrolysis of furfuryl alcohol.<sup>29,30</sup> These conversion routes are more complex than the acid hydrolysis of biomass and result in the relatively high market price of levulinic acid of ~US\$10/kg.<sup>28</sup> Cheap feedstocks are required as technological evaluations show that the raw materials are the largest cost contributor to the production process.<sup>31</sup> This is currently being addressed with investigations on cellulosic feedstocks such as lignocellulosics and municipal solid waste as suitable sources of sugars.<sup>2,32,33</sup> Other reasons for the limited manufacture of levulinic acid include the following:<sup>8,9,12,34</sup>

- Low yield. This is due to the inherent physical properties of levulinic acid which do not allow for its efficient recovery. In addition, the non-selective nature of the catalysts result in undesired side reactions and re-polymerized products at each step of the reaction pathway.
- Equipment costs. Expensive construction material for both reactor and acid recovery plant.
- High temperatures are required to convert feedstocks resulting in high heating inputs.
- Waste disposal issues or high operating costs for catalyst recovery.

In this paper, technologies for the production of levulinic acid from lignocellulosics are reviewed and some of the limitations and challenges discussed.

### Lignocellulosic feedstocks

The most abundant hexose sugar found in nature is glucose which is available in the polysaccharide form as starch or cellulose (in biomass) and in the disaccharide form as sucrose (derived from glucose and fructose). Other naturally occurring hexoses include galactose and mannose present in the hemicellulose component of biomass and fructose which along with glucose are found in many foods and are important dietary monosaccharides.

Lignocellulosics are a type of biomass, and mainly consist of: cellulose, hemicellulose, and lignin. Lignocellulosics can

be grouped into four main categories: agricultural residues (including corn stover and sugarcane bagasse), dedicated energy crops, forestry residues (including sawmill and paper mill discards), and municipal organic and paper wastes.<sup>33,35</sup> Agricultural and forestry residues have a major advantage over other lignocellulosic resources in that they have the infrastructure in place for collection, transport and processing and combined with their abundance represent a promising low cost feedstock for the production of bio-based chemicals. The composition of various lignocellulosics are detailed in Table 1 and show that variations exist between sources.<sup>36,37</sup>

In lignocellulosic materials, cellulose is ordered into fibrils which are surrounded by a matrix of lignin and hemicelluloses.<sup>38</sup> Cellulose is a high molecular weight linear polysaccharide of  $\beta(1\rightarrow4)$  linked  $\alpha$ -D-glucopyranose joined by a network of inter- and intra-molecular hydrogen bonding and van der Waals forces allowing the formation of a relatively ordered (crystalline) structure.<sup>39</sup>

In contrast to the ordered structure of cellulose, the character of the hemicellulose and lignin fluctuates with respect to the biomass type.<sup>37</sup> Hemicellulose consists of a branched structure that provides an interpenetrating matrix to cellulose through hydrogen bonds and van der Waals forces. Hemicellulose is mostly composed of xylan, though arabinan, galactan and mannan are also present, and the core structure consists of a linear backbone of  $\beta(1\rightarrow4)$  linked D-xylopyranosyl residues. Lignin is an amorphous, mono-nuclear aromatic compounds that is cross-linked to both cellulose and hemicellulose through combinations of hydrogen bonds, ionic interactions, ester and ether linkages and van der Waals interactions. The presence of lignin in lignocellulosics leads to a protective barrier that prevents plant cell destruction.<sup>37,40</sup>

As a result of the architectural features of lignocellulosics, one of the challenges of our time is to develop cost-effective

**Table 1. Chemical analysis of selected lignocellulosic sources.**

	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)
<b>Agricultural residues</b>	35–55	25–35	15–30
<b>Energy crops</b>	30–50	20–40	10–20
<b>Forestry residues</b>	40–50	25–35	20–30

fractionation procedures for the release of sugars from lignocellulosics. These sugars can then be converted to platform chemicals such as levulinic acid.

## Chemistry of levulinic acid production

Levulinic acid ( $C_5H_8O_3$ ), also known as laevulinic acid, 4-oxopentanoic acid,  $\beta$ -acetylpropionic acid and  $\gamma$ -ketovaleric acid, is a water soluble, organic compound with a ketone and carboxylic group giving it a wide range of functionality and reactivity. It is also soluble in alcohol and ether. The reactivity of levulinic acid makes it an ideal intermediate for the production of useful derivatives but unfortunately inhibits its facile recovery. The production of levulinic acid is dependent on both the feedstock and processing conditions.<sup>41</sup>

An extensive historical review of how levulinic acid has been synthesized via acid-catalyzed decomposition of feedstocks ranging from sugars (sucrose, glucose, fructose), starch (corn starch), inulin, cellulose, sawdust, woods, paper and pulp, and various crop residues (bagasse, rice hulls, corn stalks sorghum grains, cotton stems, wheat and rice straw) is provided by Girisuta.<sup>42</sup> Saeman<sup>43</sup> found that the particle size of cellulose in the range 74–840  $\mu\text{m}$  did not affect the hydrolysis reaction rate, while Sharples<sup>44</sup> found that crystallinity had an inverse relationship on the hydrolysis reaction rate.

A possible way to improve the yields and reaction rates with lignocellulosic feedstocks is through pre-treatment processes. Pre-treatment processes serve to increase the accessibility of cellulose.<sup>45–48</sup> These include methods designed to disrupt the tight packing arrangement of cellulose fibrils in the lignocellulosic structure and can include mechanical methods to reduce the particle size and increase the surface area, and explosive depressurisation processes (e.g. steam, ammonia freeze and carbon dioxide explosion) that swell and break up the fibre bundles through rupturing the weakly bound hydrogen bonding within the lignocellulosic material.<sup>49–51</sup> Some alkali treatment<sup>52,53</sup> and ionic liquids (ILs) such as N-methylmorpholine-N-oxide also serve to swell the cellulose.<sup>54,55</sup> There are also other processes that result in complete decrystallization of the cellulose component (e.g. ILs)<sup>47,56,57</sup> and those that convert the cellulose and hemicellulose into sugars (e.g. concentrated acids).<sup>45,46</sup>

The efficient and optimised production of levulinic acid requires detailed understanding of the kinetics and

mechanisms of the key reaction pathways. A number of mechanistic studies have been undertaken on the acid-catalyzed conversion of hexose sugars to HMF<sup>58,59</sup> and subsequently to levulinic acid<sup>60</sup> using nuclear magnetic resonance spectroscopy to elucidate intermediate products and to determine the reaction pathways. Proposed mechanisms of hexose sugar decomposition to HMF under acid-catalyzed conditions have been simplified and include isomerization reactions between glucose and fructose via keto-enol tautomerization with acyclic dehydration routes from the 1,2-enediol intermediate and cyclic dehydration routes from fructose.<sup>61</sup> The acyclic route is generally accepted as the prevalent mechanism based on the limited data obtained from mechanistic studies from glucose substrates<sup>61</sup> while cyclic routes are preferentially prevail from fructose substrates.<sup>62</sup> The simplified reaction pathways are illustrated in Scheme 1 and also show the two hydrolysis mechanisms for the subsequent degradation of HMF to levulinic acid.<sup>60</sup> Retro-aldol condensation products (formed by C–C bond breaking),<sup>63</sup> irreversible dehydration products from glucose such as 1,6-anhydroglucose<sup>63</sup> and cross-polymerization products that conceivably form between the numerous intermediate products have not been included in Scheme 1.

The thermochemistry of the conversion of glucose to levulinic acid through fructofuranosyl intermediates was investigated by Assary and co-workers.<sup>64</sup> They found that the first two dehydration steps are highly endothermic likely indicating these to be key steps in controlling the overall progress of the reaction, while the other steps, including the additional water elimination and rehydration to form levulinic acid, are exothermic. The dehydration reaction steps were predicted to be more favourable thermodynamically under elevated temperatures and aqueous reaction environments.<sup>64</sup>

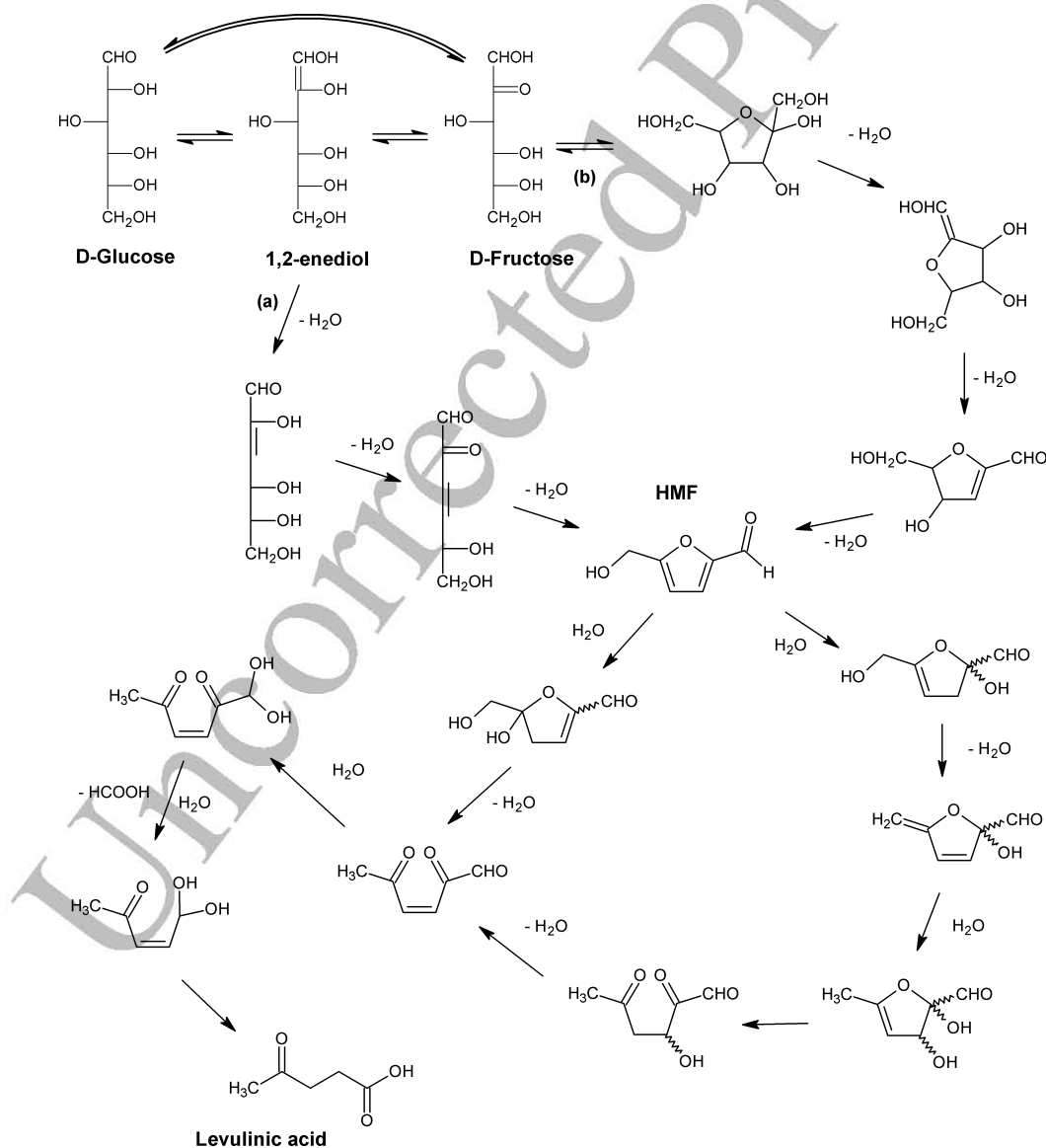
The hemicellulose and lignin components of lignocellulosics can also affect the decomposition reactions. The hexose sugars of hemicellulose can be converted to levulinic acid or other organic acids, while the pentose sugars are converted to furfural. Acetyl groups associated with some hemicellulose components also commonly form acetic acid. The acid hydrolysis process also forms various acid soluble lignin-derived components, increasing the product complexity. The simplified acid-catalyzed conversion of lignocellulosics to various liquid products is shown in Scheme 2. The

products (and intermediate products) from the decomposition of lignin (as well as cellulose and hemicellulose) can re-polymerize to undesired insoluble-polymeric materials (humins) and are not shown in Scheme 2.

In the first stage of cellulose (polyglucan) hydrolysis, the glucoside bonds between the  $\alpha$ -D-glucose units need to be broken. The mechanism for C-O-C bond cleavage in cellulose involves protonation of glucoside bonds. The proton can either attack the oxygen bond between the two glucose units or the cyclic oxygen.<sup>2</sup> In addition to these two hydrolysis pathways Mok *et al.*<sup>65</sup> proposed another pathway that produces modified cellulose that is non-reactive in nature.

The non-reactive cellulose is one limitation of using lignocellulosics in comparison to other feedstocks and highlights the importance of biomass pre-treatment to assist cellulose accessibility.<sup>66</sup>

Many kinetic studies have been conducted on the hydrolysis of various biomass materials to sugars but there are limited reports on the kinetics of levulinic acid production from glucose,<sup>41,67,68</sup> cellulose<sup>69,70</sup> and other biomass sources.<sup>7,71</sup> Saeman<sup>43</sup> was one of the first to use a systematic approach to model the hydrolysis of various wood materials to glucose and the glucose decomposition in two consecutive first-order reactions. This approach was extended to the production of



Scheme 1. Reported reaction mechanisms for the conversion of hexose sugars to levulinic acid.

levulinic acid and includes the kinetics of the formation of intermediates and by-products as shown in Scheme 3.<sup>7,41,67–69,71</sup> The kinetic modelling studies for biomass to levulinic acid suggest the reactions follow a pseudo-homogeneous (and partly irreversible) consecutive first-order reaction sequence.<sup>7,41,67–71</sup>

The reactions are assumed to be dependent on the reactant concentration ( $R_i$ ) with the rate constants ( $k_{iH}$  and  $k_{iP}$ ) typically defined by modified Arrhenius equations<sup>7,41,67–69,71</sup> using a power-law approach, including the effects of temperature ( $T$ ) and acid hydrogen ion concentration ( $A_{H^+}$ ) or pH if the hydrogen ion concentration is not quantified.<sup>70</sup> A simplified expression for the reaction rate is defined as follows:

$$\frac{dR_i}{dt} = -x(R_i)^\sigma (A_{H^+})^\varphi \left[ k_{iP} \exp\left[\frac{E_{iP}}{Rf(T)}\right] + k_{iH} \exp\left[\frac{E_{iH}}{Rf(T)}\right] \right];$$

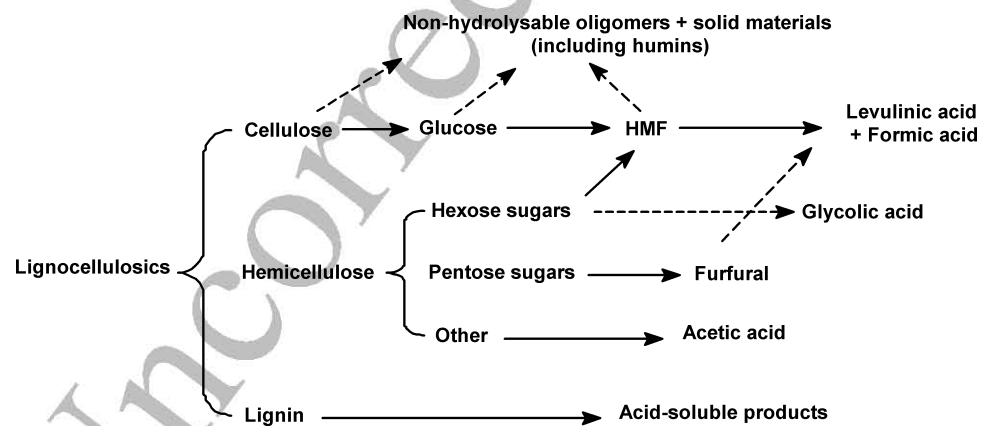
$i = 1,2,3,4$  (Equation 1)

Where  $\sigma$  and  $\varphi$  are the reaction order of the reactant and acid hydrogen ion concentrations respectively;  $E_{iP}$  and  $E_{iH}$  are the activation energy of the decomposition products and

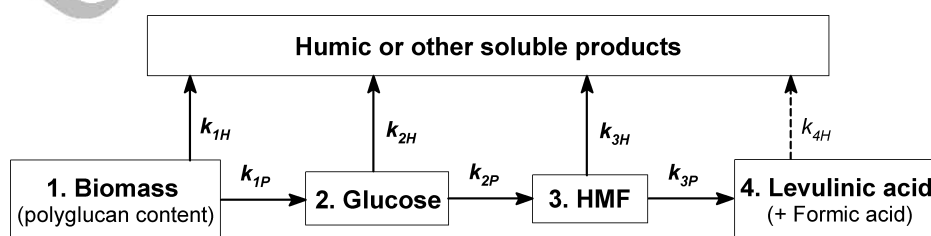
humic side reaction products respectively; and  $R$  is the universal gas constant.

Girisuta *et al.*<sup>7</sup> used a correction factor ( $x$ ) to account for the lower rate of depolymerization of hexose sugars from biomass compared to reaction rate data previously determined for pure cellulose.<sup>69</sup> The lower rate is expected to be due to the matrix of the biomass (e.g. the presence of lignin) and difference in the cellulose properties (e.g. degrees of polymerization and crystallinity). For homogeneous acid catalysis, the literature shows lower  $E_{iP}$  values to the corresponding  $E_{iH}$  indicating the reaction favours the formation of products (glucose, HMF and levulinic acid) rather than the side reactions.<sup>7,41,67–71</sup> The activation energy was also higher earlier in the reaction sequence explaining the necessity of higher temperatures required for the initial depolymerization and hydrolysis of biomass. The more structured (higher molecular weight) or crystalline nature of the cellulose component also results in higher activation energy values.<sup>44</sup>

An often overlooked pathway in the production of levulinic acid from lignocellulosics is derived from the pentose sugar content involving additional synthetic steps via the intermediate, furfural.<sup>72</sup> Typical furfural yields of 50 mol%



Scheme 2. Simplified acid-catalyzed decomposition of lignocellulosics.



Scheme 3. Reaction network for the conversion of biomass to levulinic acid.

are obtained in acid-catalyzed conversion of pentose sugars. Furfural can then be catalytically reduced to furfuryl alcohol by a well established industrial process<sup>72</sup> (yields of >95 mol%) and further acid hydrolysis of furfuryl alcohol will produce levulinic acid<sup>29</sup> in yields of up to 83 mol% or up to 93 mol% using aliphatic ketone solvents.<sup>73</sup> The reaction pathway is shown in Scheme 4. An alternative process consisting of the hydroxymethylation of furfural with formaldehyde to produce HMF can only achieve low yields (<50 mol%) and also requires the use of organic co-solvents.<sup>74</sup> The HMF can be subsequently converted to levulinic acid. This approach is often disregarded due to the processing complexity (increased operating costs) and the intermediates, furfural and furfuryl alcohol in their own rights are valuable commodity products. However, if furfural can be produced using biphasic systems as reported by Weingarten *et al.*<sup>75</sup> to obtain up to 85 mol% yields, then the process may be viable.

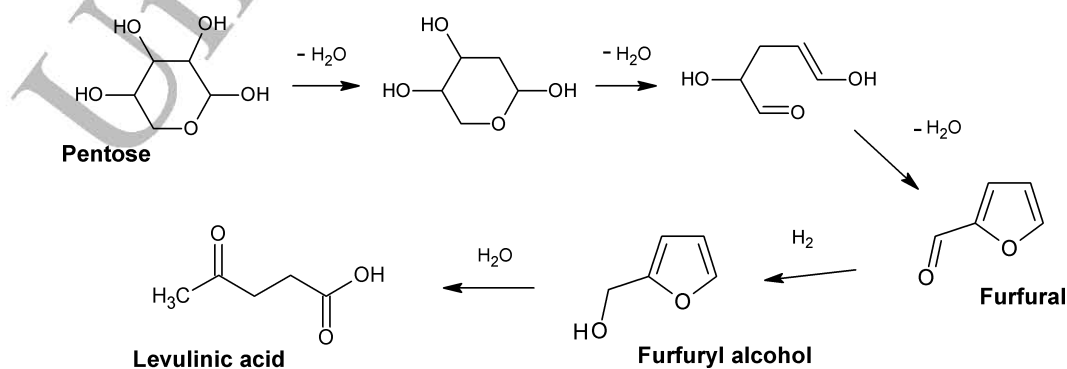
## Current technologies for the production of levulinic acid

### Homogeneous acid catalysts

The majority of research into levulinic acid production from sugars, cellulose and biomass has been conducted with mineral acid (in particular, Brønsted acids) catalysts. Cha and Hanna<sup>76</sup> found the effectiveness of dilute acids on the production of levulinic acid from sucrose were as follows  $\text{HBr} > \text{HCl} > \text{H}_2\text{SO}_4$ , which also corresponds to the magnitude of their dissociation constants (pKa);  $\text{HBr} = -9$ ,  $\text{HCl} = -8$  and  $\text{H}_2\text{SO}_4 = -3$ . However, other research indicated the highest yielding acid catalyst is dependent on both the feedstock and concentration.<sup>11,42</sup> Interestingly, while nitric acid was found

to be more effective than other strong acids in hydrolysing sugarcane bagasse to sugars and conversion of hemicellulose to furfural,<sup>77</sup> it was not as effective in producing levulinic acid, indicating acidic strength is not the most important characteristic of the catalyst. Under limited reaction conditions, Girisuta<sup>42</sup> found that nitric acid was able to convert HMF to a similar extent as other Brønsted acid catalysts, but the main products formed were formic acid, unidentified gaseous products and insoluble humins rather than levulinic acid. This may indicate the role of the anion in affecting the activity-selectivity of the reaction pathway.

A review of the possible levulinic acid yields from different cheap and readily available feedstocks (and including hexose sugars) is provided in Table 2 and show a limit of ~80 mol% yield can be obtained through optimized reaction conditions. The high levulinic acid yields shown for some lignocellulosic material in Table 2 may be distorted due to the basis considered (i.e., cellulose/hexose sugar content). The highest yields of levulinic acid result from bagasse, wheat straw and pulp. These materials would have undergone some form of pre-treatment allowing easier access to the cellulose component of the biomass. Depolymerization has long been recognized as the bottleneck for the conversion of biomass to chemical products due to limited solubility of cellulose in aqueous solutions and high temperatures required.<sup>78</sup> This shows that the biomass architecture and pre-treatment can impact favourably on cellulose accessibility and resulting process yields. The variability of the yield data also reflects the different processing conditions (i.e., heating rates), analytical techniques and reactor design employed in each of the laboratory studies. These factors will influence the ability to replicate high yields on an industrial scale.



Scheme 4. Reaction pathway for the conversion of pentose sugars to levulinic acid.



**Table 2. Yield of levulinic acid for various raw materials.**

Feed	Cellulose content (%)	Acid and concentration	Operating temperature (°C)	Yield <sup>a</sup> (mol%)	Ref.
Fructose		3.6–7.2% HCl	95	~81	79
Glucose		5% H <sub>2</sub> SO <sub>4</sub>	170	80.7	41
Starch		6% H <sub>2</sub> SO <sub>4</sub>	200	66.4	76
Paper	85	>5% H <sub>2</sub> SO <sub>4</sub>	<240	59.8	34
Pulp residues	80	1–5% H <sub>2</sub> SO <sub>4</sub>	1 <sup>st</sup> stage: 210–230 2 <sup>nd</sup> stage: 195–215	70–80	80
Wheat straw	40.4	3.5% H <sub>2</sub> SO <sub>4</sub>	210	68.8	81
	40	4.5% HCl	220	79.6	30
Sorghum grain	73.8	8% H <sub>2</sub> SO <sub>4</sub>	200	45.6	82
Bagasse	42	4.5% HCl	220	82.7	30
Water hyacinth	26.3	10% H <sub>2</sub> SO <sub>4</sub>	175	53	7

<sup>a</sup> Based on theoretical yield of the conversion of cellulose/hexose sugars.

A number of investigations have also been carried out to determine the effects of various processing conditions on reaction yields. In order of proposed importance according to Chang *et al.*<sup>81</sup> these include:

- **Acid concentration.** Reaction yields increase with acid concentration up to a critical concentration limit which depends on other processing conditions and the feedstock.<sup>30</sup> Generally too aggressive conditions lead to a higher prevalence of side reactions and re-polymerization of products and intermediates with the optimal acid concentration found to vary between 3.5 and 10 wt%.<sup>7,30,76,80–82</sup>
- **Temperature.** Generally the yield of levulinic acid from biomass increases with increasing temperatures in the range 150°C–230°C with many researchers finding an optimum temperature of 200°C–220°C.<sup>30,34,76,80–83</sup>
- **Solvent concentration.** Too much or too little amounts of solvent (water) can inhibit the hydrolysis process and the optimal concentration was also found to depend on acid concentration but generally was >90 wt%.<sup>81,84</sup>
- **Residence time.** The effect of residence time on yield was found to be dependent on the intrinsic composition of the cellulose content of the biomass source.<sup>30</sup>

Volatile acid catalysts (e.g. HCl) provide the simplest levulinic acid recovery process and involve filtering to remove solids and atmospheric/vacuum distillation and steam

stripping. This process allows 90–95% of the acid catalyst and water to be recycled to achieve levulinic acid of 95–97% purity.<sup>85,86</sup> Alternatively, the acid catalyst can be neutralized and removed as a salt but the ability to recycle catalysts is beneficial for cost-effective production processes.

For less volatile acid catalysts (e.g. H<sub>2</sub>SO<sub>4</sub>), solvent extraction, or reactive extraction separation methods have been employed as a means to improve separation and purification of levulinic acid. Reactive extraction methods using water-immiscible alcohols as both the esterifying agent and solvent removes the need for additional solvents and processing.<sup>87</sup> Furthermore it is claimed that processing (neutralization) of the reaction mixture to recover/remove the acid catalyst is not required (less waste) allowing the acid catalyst-water mixture to be recycled and the levulinate ester product is a useful chemical products in its own right. Enhanced reactive extraction methods have also been developed utilizing membranes for more efficient separation.<sup>88</sup> Simulated moving bed chromatography using multiple chromatographic columns have also been reported to recover the levulinic acid in high purity.<sup>34</sup> One drawback of homogeneous acid-catalyzed processes is the corrosive reaction conditions requiring special materials for reactor construction and chemical recovery systems increasing capital and operating costs. Also, depending on the recovery process of levulinic acid significant amounts of waste are produced causing environmental pollution.

This may be overcome by conducting the reaction in the vapour phase which will allow simple catalyst recovery and product separation.<sup>89</sup> Zeitsch<sup>90</sup> reported furfural yields of up to 95.8 mol% from pentose sugars using gaseous HCl compared to typical yields of 50 mol% obtained in a liquid acid-catalyzed process. Only HCl was investigated as the boiling point or the dew point of the water-HCl mixture was reasonably low allowing the reaction to be conducted at <160°C.

### Fluorinated solvents/acids

Fluorine being the most electronegative of all the elements with a very high ionization potential makes fluorochemistry a powerful solvent/catalyst system ideal for use in organic chemistry. Biphasic fluorinated techniques allow the separation of catalyst and reagents from the product.<sup>91,92</sup> Recently Heeres *et al.*<sup>27</sup> identified tri-fluoroacetic acid (TFA), with a pK<sub>a</sub> of 0.5, as an attractive alternative to mineral acids for the conversion of hexose sugars to levulinic acid. D-glucose gave yields of levulinic acid up to 57 mol% which Heeres *et al.*<sup>27</sup> indicated was marginally less than then 60 mol% obtained with H<sub>2</sub>SO<sub>4</sub>. It should be noted that the referenced 60 mol% yield of levulinic acid from glucose was obtained at 140°C and only 90% glucose conversion (2 h reaction time) whereas the TFA study was conducted at 180°C and half the reaction time. Other research obtained ~80 mol% yield of levulinic acid from glucose at 170°C and 1 h reaction time.<sup>41</sup> The experimental data obtained using TFA was modeled using the power law developed for H<sub>2</sub>SO<sub>4</sub> and obtained good agreement, indicating that the kinetic models developed for H<sub>2</sub>SO<sub>4</sub> can be used for TFA.<sup>27</sup> The problem with using TFA is it forms an azeotrope with water when its boiling point of

105°C is reached complicating recovery processes. However, Heeres *et al.*<sup>27</sup> indicated that the biphasic ability of fluorinated compounds can be exploited by using a TFA derivative such as heptadecafluorononanoic acid as the catalyst in the presence of a soluble solvent such as perfluorohexane. This would result in the efficient recovery and recyclability of the acid catalyst reducing operating costs.

### Solid catalysts

Heterogeneous catalysts represent a viable alternative to homogeneous catalysts and may offer an environmental advantage due to their selective and easy to handle nature, reduced equipment corrosion issues and relatively low cost if the catalyst can be easily separated and recycled.<sup>93–96</sup>

Table 3 summarises the limited studies conducted on the synthesis of levulinic acid using solid acid catalysts from various feedstocks. Low reaction yields were obtained, reaction rates were slow and prolonged reaction times were required to get reasonable quantities of levulinic acid. Girisuta<sup>42</sup> conducted adsorption experiments and found that levulinic acid can be heavily absorbed onto the catalyst surface reducing the amount of the product recovered. The use of LZV zeolite catalyst for the formation of levulinic acid from fructose achieved the highest yields of up to 43 mol%.<sup>97</sup> Corma *et al.*<sup>5</sup> are of the view that the selectivity of the zeolite catalyst to levulinic acid formation may be due to reactions occurring within the pores of the zeolite in addition to those occurring on the outer surface of the zeolite particles. As shown in Table 3 very poor results were obtained for glucose and cellulose implying that the same would be obtained with lignocellulosics.

**Table 3. Heterogeneous acid-catalyzed production of levulinic acid.**

Feed	Catalyst	Conc (wt%)	Process conditions		Yield (mol%)	Ref.
			Temp. (°C)	Time (h)		
Fructose	Amberlite IR-120	19	25	27	23.5	98
	LZY-zeolite	50	140	15	43.2	97
Glucose	Amberlite IR-120	19	25	124	5.8	98
	Clay-catalyst	3	150	24	12	99
	HY-zeolite	3	150	24	6	99
Sucrose	Amberlite IR-120	19	25	41	15.6	98
	Resin-Dowex	6.25	100	24	24	95
Cellulose	Nafion SAC-13	3	190	24	9	100
HMF	ZSM-5	5	116	2	70.0	42

While heterogeneous catalysts have not successfully been used to produce levulinic acid from sugars, they have been used to convert sugars to HMF.<sup>61,101–103</sup> High yields of HMF were able to be achieved through suppression of the HMF hydrolysis reactions by using non-aqueous solutions<sup>61,101–103</sup> and ILs (discussed later). Selected results from these studies have been detailed in Table 4. Kuster<sup>61</sup> reports the use of ion-exchange resins in the presence of dimethylsulfoxide (DMSO) and methylisobutylketone (MIBK) to obtain a 97 mol% yield of HMF from fructose. Shimizu *et al.*<sup>104</sup> used Amberlyst-15 with small particle sizes (0.05–0.15 mm) in the presence of DMSO to convert fructose in 100 mol% yield by conducting the dehydration reaction under a slight vacuum to continuously remove water which suppressed the hydrolysis of HMF to levulinic acid and condensation of intermediates. This approach and others, offer the potential for multi-stage processes using different catalysts/solvents to enable optimized and selective production of HMF from biomass and subsequent conversion to levulinic acid in high yields.

Heterogeneous catalysts combined with solvolysis reactions will aid the subsequent product separation and recovery process. The catalysts highlighted in Table 4 require low operating temperatures, and while this can minimize process energy requirements, it comes at the detriment of longer reaction times. However, for solid catalysts to be used on lignocellulosics there is the need to design new and efficient catalyst based systems.

### Other technologies

The following section highlights several alternative technologies that could be applied to the production of levulinic acid from lignocellulosics. These technologies are in their

infancy compared to the well-established homogeneous and heterogeneous acid catalysis research but show potential from application with simple sugars as the starting material. Currently these technologies would require an initial conversion step to supply the sugars but further development may allow the hydrolysis and dehydration of biomass and lignocellulosic materials to be implemented in a single reaction stage. These solvent technologies have yet to be applied to levulinic acid production but are able to produce HMF (an intermediate in the formation of levulinic acid) in high yields showing the potential that a multi-stage process will improve the overall process of converting lignocellulosics to levulinic acid.

### Biphasic media

Solvolysis has an advantage over hydrolysis in that solvents can be used to alter the properties of the reaction mixture to promote more selective reactions and due to their higher dielectric constant, allow reactions to occur at lower temperatures. Solvents can also be used in biphasic systems which allow products to be selectively isolated from the reaction mixture preventing re-polymerization reactions and improving recovery efficiency. Under laboratory conditions, such biphasic systems have been used to convert fructose to HMF in high yields with homogeneous catalysts, heterogeneous catalysts and ILs (discussed later). The solvent was utilized to suppress subsequent conversion to levulinic acid.

Roman-Leshkov *et al.*<sup>105</sup> produced HMF in 75 mol% yield from fructose in DMSO and poly(1-vinyl-2-pyrrolidinone) with HCl catalyst and an organic phase of MIBK and 2-butanol used to enhance partitioning of the reactive species. Roman-Leshkov and Dumesic<sup>106</sup> were able to improve the

**Table 4. Heterogeneous acid-catalyzed production of HMF.**

Feed	Catalyst	Conc (wt%)	Process conditions			Ref.
			Temp. (°C)	Time (h)	Yield (mol%)	
Fructose	C-ZrP <sub>2</sub> O <sub>7</sub> + water	3	110	1	45	101
	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> + DMSO	1.5	130	4	68	103
	Zeolite + MIBK	0.5	165	2	73	102
	C-ZrP <sub>2</sub> O <sub>7</sub> + MIBK	3	100	1	85	101
	IE resin + water	–	90	15	90	61
	IE resin + DMSO + MIBK	–	76	5	97	61
	Amberlyst 15 + DMSO	16.7	120	2	100	104
Glucose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> + DMSO	1.5	130	4	48	103

HMF yield from fructose to 78 mol% using tetrahydrofuran as the solvent with HCl catalyst and addition of an inorganic salt such as NaCl to improve the partitioning into the extracting phase. NaCl has also been shown to improve yields of homogeneous acid-catalyzed production of levulinic acid through an improved catalytic effect because of increase in acidity possibly due to an increase in chloride ions.<sup>85</sup> On the other hand, Chheda *et al.*<sup>107</sup> produced HMF in 87 mol% yield from fructose in DMSO without HCl catalyst and using dichloromethane as the organic phase. Other feed materials were also tested by Chheda *et al.*<sup>107</sup> but HMF yields were significantly lower from sucrose (~51 mol%), glucose (~30 mol%) and starch and cellubiose (~38 mol%). The low yields from glucose and its polymers is due to the comparatively stable (less reactive) nature of glucose resulting in less selective dehydration routes<sup>59</sup> and the conversion of polyglucans (starch and cellubiose) requires both a hydrolysis and dehydration step. Unfortunately, DMSO is a high boiling point solvent so is not suitable because of the high energy expenditure during distillation and solvent degradation.<sup>106</sup> Binder and Raines<sup>108</sup> used the cellulose solvent N,N-methylacetamide (DMA) to convert fructose with mineral acids and inorganic salts to HMF in 92 mol% yields and glucose to HMF in 81 mol% yield with the addition of chromium chloride.

The development of appropriate organic solvents is one limitation of biphasic solvent systems as small amounts of product left in the aqueous phase reduces yields especially if the partitioning is inadequate. To overcome low partitioning large amounts of solvent are used which would necessitate high energy expenditures in the subsequent product recovery stage.<sup>107</sup> Likewise, these multi-solvent processes would require a relatively complex plant design which may increase capital costs.

### Supercritical fluids

Supercritical fluids are another class of solvents with interesting features that can be used to enable more selective reactions and efficient separation of products. Supercritical fluids exhibit both acidic and basic properties. A review of the use of sub- and supercritical water to produce HMF from sugars, gave low yields.<sup>21</sup> However, Bicker *et al.*<sup>109</sup> was able to achieve >75 mol% yield of HMF from fructose using supercritical acetone.

Supercritical carbon dioxide has also been used to continuously extract furfural from the acid hydrolysis of biomass in higher yields (~90 mol%) than conventional reactions.<sup>110</sup> The supercritical fluid acts as a solvent to separate the product from the reaction mixture to suppress unwanted side reactions that would otherwise reduce the yield. However, the process requires substantially higher operating pressures than conventional processes warranting higher equipment costs.

Research on supercritical fluids should concentrate on identifying fluids that can allow selective extraction of HMF from the reaction mixture. This would limit contamination of low boiling organic products (e.g. formic acid, acetic acid and furfural) and limit re-polymerization reactions. HMF could then be stepwise converted to levulinic acid in a more selective secondary process.

### Ionic liquids

ILs are molten salts that are liquid at room temperature, are an important class of chemicals that can act as both a solvent and catalyst.<sup>111,112</sup> Other attractive properties of ILs include low vapour pressure, non-flammability and thermal stability.<sup>112</sup> ILs offer similar advantages to heterogeneous catalysts in that they can usually be easily separated from the reaction mixture for reuse and retain high activity plus they offer the advantage of allowing the reaction process to be conducted at much lower temperatures ( $\leq 100^\circ\text{C}$ ).<sup>113</sup>

While ILs have yet to be used in the synthesis of levulinic acid, they have been used to produce HMF in high yields from sugars in conjunction with mineral or heterogeneous acid catalysts, metal salts and co-solvents as summarised in Table 5. Moreau *et al.*<sup>111</sup> was able to achieve a 92 mol% yield of HMF from fructose dissolved in 1-H-3-methylimidazolium chloride ([Hmim]Cl) and diethylether (DEE) as co-solvent with Amberlyst-15 in a relatively short reaction time of 45 min. Similarly Lima *et al.*<sup>114</sup> was able to achieve a 88 mol% yield of HMF from fructose dissolved in 1-ethyl-3-methylimidazolium hydrogen sulphate ([Emim]HSO<sub>4</sub>) acting as the acidic catalyst and MIBK as the co-solvent in a 30 min reaction. Other IL systems were also able to achieve high HMF yields from fructose though requiring longer reaction times of >3 h.<sup>115,116</sup> As ILs are expensive and difficult to purify, a simple solvent catalyst system would be preferred rather than the multi-catalyst/solvent processes described above. Hu *et al.*<sup>117</sup> reported a simple choline chloride-citric acid based

**Table 5. Production of HMF using ionic liquids.**

Feed	Catalyst	IL/Solvents	Temp. (°C)	Time	Yield (% HMF)	Ref.
Fructose	Amberlyst-15	[Hmim]Cl + DEE	90	45 min	92	111
	[Emim]HSO <sub>4</sub>	MIBK	100	30 min	88	114
	ChoCl/CA	Ethyl acetate	80	1 h	91	117
	NHC/Cr	[Bmim]Cl + DEE	100	6 h	99	116
	H <sub>2</sub> SO <sub>4</sub> + KI	DMA	100	5 h	92	108
	H <sub>2</sub> SO <sub>4</sub>	DMA + [Emim]Cl	100	2 h	84	108
Glucose	CrCl <sub>2</sub> /CrCl <sub>3</sub>	[Emim]Cl	80	3 h	70	20
	CrCl <sub>3</sub>	[Bmim]Cl	100 (MI)	1 min	91	118
	CrCl <sub>3</sub>	[Bmim]Cl + toluene	100	4 h	91	114
	NHC/Cr	[Bmim]Cl + DEE	100	6 h	81	116
	CrCl <sub>2</sub> + HCl + NaBr	DMA	100	5 h	81	108
	CrCl <sub>2</sub>	DMA + [Emim]Cl	100	6 h	67	108
Cellulbiose	CrCl <sub>3</sub>	[Bmim]Cl + MIBK	100	4 h	50	114
Cellulose	CrCl <sub>3</sub>	[Bmim]Cl	200 (MI)	2 min	61	118,121
	CrCl <sub>2</sub> /CuCl <sub>2</sub>	[Emim]Cl	120	8 h	58	122
	CrCl <sub>2</sub> + HCl + LiCl	DMA + [Emim]Cl	140	2 h	54	108
Cornstover	CrCl <sub>3</sub> + HCl + LiCl	DMA + [Emim]Cl	140	2 h	48	108
Wood	CrCl <sub>3</sub>	[Bmim]Cl	200 (MI)	3 min	~52	121
	CrCl <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	[Bmim]Cl	200	1 h	~35	121

IL (ChoCl/CA) and ethyl acetate biphasic system that gave more than 90 mol% HMF yields from fructose in 1 h. The IL was cheaply synthesized from renewable materials and easily recycled, however the selectivity of the system was not tested on other sugars or polymers.<sup>117</sup>

Binder and Raines<sup>108</sup> used DMA with [Emim]Cl to convert fructose with mineral acids to HMF in 84 mol% yields and glucose to HMF in 67 mol% yield with chromium chloride. These yields were lower than that achieved without the use of [Emim]Cl as co-solvent. Two IL systems were able to achieve high yields of HMF with both glucose and fructose.<sup>114,116</sup> Yong *et al.*<sup>116</sup> used [Bmim]Cl and DEE catalyzed by N-heterocyclic carbene (NHC) chromium complexes to convert fructose and glucose to HMF in 99 mol% and 81 mol% yields respectively. Lima *et al.*<sup>114</sup> also used [Bmim]Cl but with toluene co-solvent and chromium chloride catalyst to convert glucose to HMF in 91 mol% yield. Longer reaction times (>4 h) were necessary to produce high yields from glucose. On the other hand, Li *et al.*<sup>118</sup> was able to convert glucose to HMF in 91 mol% yield in [Bmim]Cl with chromium chloride but under microwave irradiation

(MI) for 1 min at ~~400 W~~. The use of MI is known to accelerate organic reactions and improve catalytic processes especially in the hydrolysis and dehydration of sugars.<sup>119</sup> MI results in dielectric heating where the solvent absorbs microwave energy and converts it into heat in a more efficient and rapid fashion compared to conventional heating. This can cause superheating, selective heating of reagents/catalysts, re-orientation of dipolar molecules to lower the activation energy resulting in reactivity enhancements and the elimination of wall heating effects.<sup>120</sup>

No IL system has yet been reported to produce high yields of HMF from cellulose or biomass possibly implying that an initial depolymerization/hydrolysis/fractionation step is required. The highest HMF yields from cellulose or biomass were achieved with chromium chloride dissolved in [Bmim]Cl under MI.<sup>118,121</sup> Interestingly, while a 62 mol% yield of HMF was obtained for cellulose, there remained a ~20% un-reactive carbohydrate component in the reaction mixture. This highlights the need for further development of IL systems to ensure high selectivity when processing lignocellulosic materials.

The dissolution of metal salts in the IL appeared to play a role in both stabilizing the HMF product and assisting proton transfer to selectively convert the sugars via cyclic routes to HMF rather than the acyclic route typical of acid catalyzed aqueous processes.<sup>20</sup> The optimum IL-metal salt complex is dependent on feedstock but the results show the IL-catalyst system can be tuned, opening the possibility for a combination of ILs (and/or metal salts) to be used to optimise yields from various feedstocks.<sup>108,122</sup>

On the provision that additional co-solvents are not required, the recovery of HMF in a reaction-distillation process would be theoretically relatively simple due to the advantage of ILs having little vapor pressure and HMF having a low boiling point.<sup>118</sup> While attractive, the use of ILs in the production of bio-chemicals is likely to be a long term prospect as several key limitations need to be overcome including reducing the cost of ILs and developing efficient processes for the separation and recovery of ILs, co-solvents and metal salts for recycling.<sup>123</sup> The use of ILs in conjunction with solid catalysts showed that the stability of the solid catalysts in the solvent was an important issue that governs the choice of IL.<sup>124</sup> The use of metal salts like chromium chloride also pose a potential health risk introducing further processing complications.<sup>114</sup> The use of MI in combination with ILs show potential because microwave effects are more pronounced on polar materials. The practical issues of implementing MI on an industrial scale need to be addressed if such a technology is to be used in the near future.

As with conventional acid hydrolysed processes, IL based processes that are designed to produce HMF from the hexose component of lignocellulosics will also convert the pentose sugars to other products such as furfural in significant yields.<sup>108,114,121,125</sup> The co-production of other valuable commodities such as furfural would contribute to a sustainable and cost-effective process by greater utilisation of the feedstock.

### Manufacture of levulinic acid

The wide spread application of bio-based products such as levulinic acid requires the production process to be economically viable, the existence of sizable markets, and consumer acceptance of bio-based products. Bio-based products need to be functionally similar to the petroleum products they are

replacing placing importance on quality control. However, the biodegradability and biocompatibility properties of bio-based products compared to hydrocarbon-derived products should improve their marketability.<sup>126</sup>

The development of production methods has progressed from batch processes able to achieve <50% of the theoretical yield of levulinic acid to continuous processes incorporating recycling and utilizing multi-stages to optimize processing conditions to improve the yields to ~80% of the theoretical limit. The most promising commercial process utilises the Biofine™ technology developed by Fitzpatrick<sup>80</sup> and involves a two-stage acid-catalyzed reaction process to optimize process conditions.<sup>12</sup> In the first plug flow reactor the feed is dehydrated to HMF at between 210–230°C (>3 MPa) for less than 30 s. Levulinic acid is produced in the second reactor at 195–215°C (~1.5 MPa) for 15 to 30 min. The reaction conditions in the second reactor are such that formic acid and furfural are kept in the vapour phase to allow simple separation of these products. The variation in reactor volumes (residence times) reflects the fast cellulose conversion into sugars and subsequent slower sugar conversion into levulinic acid and the reactor system design minimizes conditions amenable to side product formation.

Lignocellulosics are an extremely cheap feedstock at <5% of the cost compared to maleic anhydride which is the main feedstock used to produce analytical grade levulinic acid of high purity in use today. So, if lignocellulosic materials can be used the market price can be considerably reduced. Utilizing low cost feedstocks such as lignocellulosics or cellulose-rich waste streams, Fitzpatrick<sup>127</sup> suggests production costs of levulinic acid can be reduced to <US\$0.2/kg by expanding production of the Biofine™ process to >1000 t/day. However these costs do not include the recovery of capital investment.

### Concluding remarks

The production of chemicals from biomass represents a major challenge because of the complex nature of the biomass substrate and the presence of non-cellulose components. Also, as the conversion reaction of biomass to levulinic acid proceeds through a number of pathways involving multiple steps and intermediates, a multi-stage process with individual synthetic steps optimized for high yields may provide the key to improving overall process

yields and efficiency. Although multi-stage processes may be more complex, continuous processes and optimized reactor designs can be very effective in minimizing labour, maintenance and energy costs associated with comparable batch operations. Additionally, the development of more selective catalysts remains a key technical barrier to improve existing and new catalyst based systems including those detailed in this review. Heterogeneous catalysts offer the greatest potential due to their simple and energy efficient separation, reusable nature, limited corrosion and waste disposal issues ~~but development needs to overcome the limited yield and selectivity or temperature that can currently be achieved.~~

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**Darryn W. Rackemann**

Mr Darryn Rackemann is a process engineering research fellow at Sugar Research and Innovation, Centre for Tropical Crops and Biocommodities, Queensland University of Technology, Brisbane Australia. He has over 10 years R&D experience in the cane sugar production industry and has a Masters in

Chemical Engineering from the James Cook University (2005) on heat and mass transfer in crystallization unit operations. Mr Rackemann is currently conducting research looking at environmentally friendly and efficient solvolysis processes to target bio-chemical products (e.g. platform chemicals and biofuels) from lignocellulosics.

**William O.S. Doherty**

Dr Bill Doherty (PhD 1983, University of East London) is an Associate Professor and Team Leader of Processing Chemistry at Sugar Research and Innovation, Centre for Tropical Crops and Biocommodities, Queensland University of Technology, Brisbane Australia. He has authored and co-authored over 80 publications in the areas of, colloidal science, synthesis of polymers and biopolymers, flocculation/coagulation, solid-state reactions, surface chemistry and the physical chemistry of polyelectrolytes. Dr Doherty is currently involved in the development of new biopolymers, biomaterials and composites from biomass. Specific research activities within Dr Doherty's research group include, the use of delignification/dissolution agents (e.g. tailor-made ionic liquids, conventional pulping/thermal technology) for the fractionation/pretreatment of biomass so that its components can be used in the developments of resins, chemicals, biofuels, biodegradable blends, biodegradable blown films and lignin-based water soluble coatings.