Levulinic Acid as a Catalyst for the Production of 5-Hydroxymethylfurfural and Furfural from Lignocellulose Biomass

Bhogeswararao Seemala, Victoria Haritos, and Akshat Tanksale*^[a]

Levulinic acid (LA) was used as a catalyst for the first time to produce 5-hydroxymethylfurfural (5-HMF) and furfural (FAL) from pinewood and eucalyptus sawdust in a mono- or biphasic solvent system. 2-Methyltetrahydrofuran was used as a co-solvent with water in different ratios and temperatures (140– 200 °C). Highest yields of 5-HMF and FAL were obtained at 180 °C and 2 h reaction time; however, at 160 °C, high yields of C_6 and C_5 sugars were obtained. Both hydrolysis and dehydration steps were accelerated in the MTHF/water biphasic

Introduction

Depletion of petrochemical resources coupled with growing concerns about climate change has prompted investigation of lignocellulosic biomass utilisation for the production of value-added chemicals and biofuels.^[1] Lignocellulose biomass is an attractive feedstock because it is the most abundant renewable carbon resource. However, pre-treatment of lignocellulose remains one of the main challenges for the conversion of lignocellulose into desirable products.

Therefore, a process that requires minimal pre-treatment is highly desirable.^[2] Conversion of lignocellulose into furan derivatives, particularly 5-hydroxymethylfurfural (5-HMF) and furfural (FAL) are of high interest because they may be used as feedstock for liquid fuels and other important chemicals such as organic green solvents and high-volume plastics.^[3] Generally, conversion of lignocellulose into chemicals occurs through multiple steps: first by cleaving ester bonds between hemicellulose and lignin to release cellulose chain, followed by hydrolysis of hemicellulose and cellulose into monomer and further acid-dehydration of monosaccharides into value-added chemicals.^[4] 5-HMF is a platform chemical with its derivatives levulinic acid (LA, produced through furan ring opening), 2,5-furan dicarboxylic acid (by oxidation), dimethylfuran (by hydrogenolysis) and dihydroxymethylfuran (C=O group hydrogenation).^[5] FAL is a source of furfuryl alcohol, tetrahydrofurfurylalcohol, methylfuran and tetrahydrofuran.^[6] Both 5-HMF and FAL may be used as alternative source for the synthesis of C₆ and C₅

 [a] Dr. B. Seemala, Prof. V. Haritos, Dr. A. Tanksale Catalysis for Green Chemicals Group Department of Chemical Engineering Monash University Clayton, VIC 3800 (Australia) Fax: (+61) 3-9905-5686 E-mail: akshat.tanksale@monash.edu system compared to pure aqueous phase. In particular, 1:2 w/ w ratio of MTHF/water resulted in the highest yield of 5-HMF and FAL, whereas 2:1 w/w ratio showed highest yield of C₆ and C₅ sugars. Increasing the ratio of MTHF/water resulted in a higher fraction of dehydrated products extracted into the organic phase. LA as a catalyst is beneficial because it is miscible in both the phases and the presence of LA favours the equilibrium towards 5-HMF production.

liquid alkanes respectively, through two-step process such as furan ring opening followed by hydrodeoxygenation reaction.^[4c, 5b, 7] The process for the production of FAL from xylose is already industrialised. However, the production of 5-HMF from glucose is more difficult because this step requires isomerization of glucose molecule into fructose followed by dehydration of fructose into 5-HMF, which is limited by equilibrium conversion at both the steps.^[8] Moreover, 5-HMF may rehydrate into levulinic acid in aqueous conditions. Many attempts have been made for selective synthesis of 5-HMF with metal chlorides, bases and inorganic acids, however, separation process of those reagents are not yet clear.^[9] Ionic liquids have also been tried in the synthesis of 5-HMF and FAL with high yields, however, separation and cost of those reagents are not favourable for commercial process.^[10] Thermochemical process is efficient in depolymerization of lignocellulose, however, at higher temperature the conditions suppress product selectivity and yield. Temperatures in excess of 200 °C and acidic conditions are usually required to synthesise 5-HMF from lignocellulose but under these conditions formation of humins through condensation of C₆ and C₅ sugars with 5-HMF and FAL, and self-condensation of furan products are major limiting factors.^[11]

5-HMF and FAL product selectivity can be improved by rational selection of the solvent. Dimethylsulfoxide (DMSO) showed positive effects on increasing the final yields of 5-HMF and also suppressed the unwanted side products because of its high boiling point. However, the stability of DMSO in acidic medium during the reaction is low and the separation of 5-HMF and FAL is difficult.^[12] Water-immiscible organic solvents in the biphasic systems play an important role of extracting 5-HMF from aqueous phase. However, most of the solvents show poor partitioning of 5-HMF into the organic phase.^[5b] In the present work, remarkable results were obtained with 2-

Wiley Online Library



methyltetrahydrofuran (MTHF) and toluene as solvents with water for hydrolysis-dehydration of lignocellulose. Simeó et al. claimed that the physical properties of MTHF are similar to those of toluene, however, MTHF can be derived from renewable resources (FAL to MTHF), but toluene mostly from petrochemicals.^[13] MTHF has been also proven as a promising alternative solvent for environmentally benign synthesis strategies such as the synthesis of Grignard reagents and lithium aluminium hydride catalysts as well as carbon-carbon (C-C) coupling reactions.^[14] Owing to its low solubility in water, better stability, and high boiling point compared to tetrahydrofuran (THF), it favours easy recovery of the final products into the organic phase.^[1f,5c,15] In the present work, we report a new strategy to produce 5-HMF and FAL by using LA as a catalyst for the first time. LA is completely miscible in MTHF whereas it is immiscible in toluene. Pinus radiata (pinewood) and Eucalyptus regnans sawdust was used as feedstock in a mono- or biphasic solvent system. MTHF and toluene were used as co-solvents with water in different ratios at a temperature of 160–200 °C. The use of LA as a catalyst in a biphasic system is particularly advantageous because of (i) better control of the side reactions to achieve high yield of 5-HMF; (ii) easier extraction of desirable compounds in the organic phase; (iii) higher feasibility of the product mixture to be upgraded into chemicals and fuels; and (iv) absence of inorganic salts and acids. LA and MTHF both can be potentially produced from biomass, making the processes greener.

Results and Discussion

In Table 1 the effects of MTHF/water ratio in the biphasic system (w/w ratio = 4:1, 2:1, 1:1, 1:2 and 1:4) at 180 °C after 15 min reaction time are shown. The maximum mass conversion achieved was 45.3 %. As LA is a weak acid (pK_a = 4.17), it is likely to catalyse the cleavage of weak glycosidic ether bonds and hydrogen bonds between cellulose, hemicellulose and lignin leading to deconstruction of lignocellulose.^[16] The partition coefficient of LA in MTHF/water at equilibrium is 1.08. Although LA is completely miscible in MTHF, pure MTHF as a sol-

vent was not active for the conversion of pinewood sawdust (Table 1, experiment no.1). Cello-oligomers and hemi-monomers concentrations increased with increasing water content from 4:1 to 2:1 MTHF/water w/w ratio. The cello-oligomers molar yield was equal to 10.5% and 22.8% in 4:1 and 2:1 MTHF/H₂O ratios, respectively, based on 41.7 wt% cellulose content in pinewood,^[17] which is one of the highest yield in just 15 min reaction time.[18] Increasing the aqueous phase composition to 1:1 and 1:2 w/w ratios resulted in marginal decrease in the yield of C_6 and C_5 sugars (experiment nos. 5–7, respectively). Yields of dehydration products enhanced with increased water composition, with maximum concentration of 5-HMF and FAL obtained at 1:2 ratio of MTHF/water, which was more than a factor of five increase over their production at 4:1 ratio. Increasing the water content enhanced the polarity of the system thereby accelerating the cleavage of glycosidic ether bonds and enhanced hydrolysis step. Further increasing the ratio of aqueous phase to 1:4 suppressed the 5-HMF amounts significantly, attributed to the rehydration conversion of 5-HMF into LA. This conversion is caused by a higher fraction of 5-HMF and FAL in the aqueous phase. The percentage of 5-HMF and FAL in the organic phase dropped from 94% and 99% in the 4:1 MTHF/water mixture to only 5.6% and 16.3%, respectively, in the 1:4 mixture. Condensed products can also be formed by increasing the amount of the water media because of increase in the source of hydrogen ions in the aqueous phase. Weingarten et al. also observed that increasing the amount of water in the solvent decreased the reaction rate.^[19] Since increasing the fraction of water in the solvent mixture shifted the distribution of 5-HMF and FAL into the aqueous phase, the extraction and purification of these products would require an additional separation process. Usually, the polar phase is used to dissolve and convert the sugars, and the less polar or polar aprotic phase extracts the reactive products or intermediates such as 5-HMF and FAL and prevents further exposure to acidic protons in the polar phase.^[19] Although the LA catalyst is soluble in both MTHF and water, the difference in polarity of the solvents enables different abilities to transfer the hydrogen to reactants and, therefore, can

Exp. no.	Solvent ratio (MTHF/H ₂ O w/w ratio)	Concentration				Distribution of product in organic phase [wt%]		X [%]
	, <u>,</u>	Cello-oligomers	Hemi- monomers	5-HMF	FAL	5-HMF	FAL	
1	only MTHF	230	100	ND	ND	_	-	4.5
2	4:1	1904	498	56.8	61	94.0	99.0	25.2
3	2:1	4440	3350	168	158	74.0	92.6	45.3
4	2:1 ^[b]	3213	2450	375	432	78.5	92.5	41.8
5	1:1	2196	3090	307	288	71.5	90.0	40.7
6	1:1 ^[b]	1834	2450	585	792	73.5	91.3	40.6
7	1:2	1878	2530	353	417	52.5	81.5	38.0
8	1:4	1525	2310	200	133	5.6	16.3	36.2
9	1:1	756	1020	692	596	4.6	76.6	24.0
	toluene/water							

ChemCatChem 2016, 8, 640-647



affect the catalytic behaviour by changing the solvent ratio. 95% of LA was found in the organic phase during the reaction in 4:1 solvent ratio, and reducing the MTHF/water ratio to 2:1, 1:1, 1:2 and 1:4 reduced the catalyst amount in the organic phase to 73.5, 55.9, 44.4 and 14.4%, respectively. Therefore, the quantity of acidic protons and the polarity in the aqueous phase increased with increasing water content, which could effectively facilitate the depolymerisation of lignocellulose. Lower polarity of pure MTHF and 4:1 ratio of MTHF/water resulted in lower yields of desirable products. A comparison of the C₆ and C₅ products yields in the non-stirred and stirred reactors under identical operating conditions is shown in Table 1 (experiment no. 4 and 6). The mass conversion of pinewood sawdust and sugars yield was not influenced by stirring, which suggests that the hydrolysis reaction was kinetically controlled. However, the final yields of 5-HMF and FAL increased two- to three-fold with stirring, which suggests that the rate of mass transfer of 5-HMF and FAL from aqueous phase to organic phase was enhanced by stirring, thereby shifting the equilibrium of sugar monomer dehydration.

In comparison to the MTHF/water (1:1) mixture, the toluene/ water (1:1) mixture resulted in an increased yield of both 5-HMF and FAL by over two-fold (Table 1 experiment no. 9). Maximum 5-HMF molar yield of 7.4% was achieved in the toluene/ water (1:1) mixture compared to only 3.1% molar yield in the MTHF/water (1:1) mixture after 15 min reaction time. This suggests that toluene dissolved the lignin fraction of the biomass and exposed hemicellulose and cellulose to acidic protons in the aqueous media. Moreover, the LA catalyst is insoluble in toluene; therefore a high concentration of acid in the aqueous phase enhanced the dehydration reaction and also shifts the equilibrium towards formation of 5-HMF in aqueous phase. Since FAL has lower solubility in water as compared to 5-HMF, 76.6% of FAL was extracted into the toluene phase. However, < 5% of the 5-HMF was obtained in the toluene phase; whereas in comparison, >70% of the 5-HMF partitioned into the MTHF phase in the MTHF/water (1:1) mixture.

MTHF/water was chosen for further activity studies because it is greener than toluene/water and 1:1 ratio was selected because it resulted in higher yields of sugar monomers and furanic compounds. In Table 2 the effect of initial concentration of feedstock and LA-catalyst in (1:1) MTHF/water solvent on the conversion of lignocellulose at 180 °C is shown. The feed-

Table 2. Effect of varying the amount of solvent. ^[a]									
MTHF/H ₂ O [g]	Concentration Distribution of product in $[mg L^{-1}]$ organic phase $[wt \%]$					X [%]			
	005	490	770	272	42.0	28.0	22.0		
5:5	885	489	//8	372	43.9	28.9	33.8		
10:10	1103	1280	897	495	70.4	90.9	40.7		
15:15	903	1520	654	384	76.3	93.2	36.5		
20:20	486	768	529	269	66.9	87.5	24.2		
[a] Reaction conditions: Pinewood = 0.4 g, solvent = MTHF/water, LA catalyst = 0.1 g, reaction temperature = $180 \degree C$, reaction time = 1 h. Cello-oligomers (C-ol) = cellopentose + cellotettrose + cellotriose + cellobiose + glu-									

cose; hemi-monomers (H-ol) = xylose + arabinose + mannose.

stock and LA catalyst loading was kept constant at 0.4 g and 0.1 g, respectively, whereas the total volume of the solvent was varied from 10 g to 40 g, keeping the reaction time constant at 15 min. Increasing the total solvent amount from 10 g to 20 g resulted in an increase in the mass conversion and the mass yield of both cello- and hemi-sugars (from 8.9 to 22.1 mg and 4.9 to 25.9 mg, respectively). Particularly, 30 g of MTHF/ water (1:1) solvent system yielded higher amounts of both cello-oligomers and hemi-monomers at 903 and 1520 mg L^{-1} (mass yield = 27.1 and 45.6 mg, respectively). Moreover, more than 76% and 93% of 5-HMF and FAL, respectively, were recovered into the organic phase. However, further increasing the solvent amount to 40 g reduced the mass conversion and the yield of the products. Lowering the concentration of LAcatalyst had a negative influence on the depolymerisation of lignocellulosic biomass. Effect of catalyst loading is shown in Table 3. Increasing the catalyst amount showed positive effect

Table 3. Influence of amount of LA catalyst on pinewood conversion. ^[a]									
Exp. no.	Levulinic acid [g]	Concentration Mass [mg L ⁻¹] conv. [9							
		C-ol	H-ol	5-HMF	FAL				
1	NIL	1175	400	35	40	18.5			
2	0.05	1646	2300	184	173	31.8			
3	0.10	2196	3090	307	288	40.7			
4	0.15	2433	3080	715	692	42.6			
[a] Reaction conditions: Pinewood = 0.4 g, solvent (MTHF/water, 1:1 w/ w) = 20 g, reaction temperature = $180 \degree C$, reaction time = 15 min. Cello- oligomers (C-ol) = cellopentose + cellotettrose + cellotriose + cellobiose + glucose; hemi-monomers (H-ol) = xylose + arabinose + mannose. NIL = no LA added.									

on the furan products, indicating that the reaction was mass transfer limited. 5-HMF and FAL concentrations increased by more than a factor of two when LA-catalyst loading was increased from 0.100 g to 0.150 g, whereas sugar concentrations increased marginally. This is believed to be due to increase in the dehydration step, which is favourable at higher concentration of acid at low reaction temperatures. Similar effect has been observed with inorganic acids.^[9d]

To find out the optimum temperature, the reaction was conducted at four different temperatures: 140, 160, 180 and 200 °C (Table 4). As the temperature increased from 140 to 160°C, the yield of C₆ sugars increased to nearly four times with marginal increase in the yields of C₅ sugars, 5-HMF and FAL. Further increasing the temperature to 180°C resulted in remarkable increase in 5-HMF (to 307 mg L^{-1}) with reduction in the yield of cello-oligomers. Yield of FAL and hemi-monomers also increased remarkably. Increasing the reaction temperature to 200 °C resulted in increase in the yield of both the furanic products with lower yields of both cello-oligomers and hemimonomers (Table 4, experiment no. 3 and 4). Even though the yields of furanic compounds were higher, the overall selectivity of the desirable products (sugars + furans) was lower at 200 °C. At this temperature the reaction mixture turned dark (Figure 1), which may be caused by the formation of humins



Table 4. Effect of temperature on pinewood conversion. ^[a]								
Exp. no.	Temp. [°C]	Concentration [mg L ⁻¹] Cello-oligomers Hemi-monomers 5-HMF FAL						
1	140	1002	1704	18	22.1	21		
2	160	3907	1830	53	66	33		
3	180	2196	3090	307	288	40.7		
4	200	1141	1902	803	535	45		

[a] Reaction conditions: Pinewood = 0.4 g, solvent (MTHF/water, 1:1 w/w) = 20 g, LA catalyst = 0.1 g, reaction time = 15 min. Cello-oligomers = cellopentose + cellotet-trose + cellotriose + cellobiose + glucose; hemi-monomers = xylose + arabinose + mannose.



Figure 1. Reaction mixtures at different temperatures after reaction a) 140 °C, b) 160 °C, c) 180 °C, d) 200 °C; pinewood = 0.4 g, solvent (MTHF/ water, 1:1 w/w) = 20 g, LA catalyst = 0.1 g, reaction time = 15 min.

as by-products. Normally, humins can form through the selfcondensation of furan products and also condensation between the 5-HMF and FAL with sugars at temperatures above 180 °C in highly acidic conditions. Even though the initial reaction conditions were not highly acidic at 200 °C, acids could be generated in situ by depolymerisation of lignocellulose, which would favour the condensation reactions.^[1f]

In Figure 2a the extent of the reaction as a function of time in aqueous medium with LA catalyst at 160°C is shown. If using pure water as a solvent, C₆ sugars concentration showed a peak at 30 min (at 1081 mg L^{-1}), whereas C₅ sugars concentration showed a plateau at approximately 120 min (at 2090 mg L⁻¹). 5-HMF and FAL concentrations increased linearly for the duration of study. This suggests that the rate of depolymerisation was the limiting step and is limited by the low temperature. In comparison to the aqueous media, the MTHF/ water biphasic system with LA-catalyst resulted in higher yield and selectivity of sugars and furans at 160 °C (Figure 2b). The depolymerisation step was promoted in the biphasic system with subsequent hydrolysis-dehydration into C_6 sugars and furans. C_6 sugars decreased from the maximum of 3957 mg L⁻¹ at 15 min to approximately 2000 mg L^{-1} at 120 min, whereas HMF yields increased linearly from 50 mg L^{-1} to 447 mg L^{-1} at the respective times.

 C_5 sugars concentration increased from $1700\ mg\,L^{-1}$ at 15 min to 3150 mg L^{-1} at 60 min. Therefore it can be concluded that even though the reaction rate increased in the bipha-

sic system, it was still limited by the hydrolysis step at 160 °C. An advantage of the biphasic system was that more than 70% of the furan compounds were extracted into the organic phase that resulted in higher accessibility of aqueous acidic protons to polymeric sugars, which favoured the depolymerisation step. Lange et al. and Cai et al. also reported that pure aqueous system with dilute mineral acids typically suffers from low 5-HMF yields.^[20]

At 180 °C (Figure 3 (a)), dehydration of sugar monomers was favoured over hydrolysis of oligosaccharides, resulting in higher concentrations of 5-HMF and FAL (1186 and 536 mg L^{-1} at 120 min, respectively)



Figure 2. Effect of the solvent system on the conversion of pinewood sawdust to 5-HMF and chemicals using a) only water as solvent, b) MTHF/water (1:1 w/w) co-solvent system; pinewood = 0.4 g, solvent = 20 g, LA catalyst = 0.1 g, reaction temperature = 160 °C. (\Box) Cello-oligomers, (\bigcirc) Hemi-oligomers, (\blacktriangle) 5-HMF, (\checkmark) FAL. The bullet points are results from separate runs and the solid lines are fitted curves to illustrate the trends.

whereas the cello-oligomers and hemi-monomers concentration reduced to 865 and 477 mg L⁻¹, respectively. This results in 5-HMF molar yield of 18.3%. The rate of dehydration reaction further increased at 200 °C as observed from the rapid increase in concentration of 5-HMF and FAL to 1350 and 643 mg L⁻¹, respectively, at 60 min (Figure 3 (b)). This results in 5-HMF molar yield of 20.8%. However, at this temperature, the



Figure 3. Effect of temperature on the conversion of pinewood saw dust to 5-HMF and chemicals at a) 180 and b) 200 °C, pinewood = 0.4 g, solvent (MTHF/water, 1:1 w/w) = 20 g, LA = 0.1 g. (\Box) Cello-oligomers, (\bigcirc) Hemi-oligomers, (\blacktriangle) 5-HMF, (\blacksquare) FAL, (\blacksquare) levulinic acid. The bullet points are the results from separate runs and the solid lines are fitted curves to illustrate the trends.

desirable products were lost to humins formation at longer residence time as the reaction mixture turned to dark brown after 120 min (Figure 1) suggesting that humins formed through self-condensation of furans or condensation of furans CHEMCATCHEM Full Papers

with sugar molecules.^[20b, 21] Long residence time and high temperature also favoured LA production. The concentration of LA, excluding the LA catalysis amount, increased linearly at 180°C. The fraction of 5-HMF that is present in the aqueous phase is susceptible to rehydration into LA,^[21] and since this reaction mixture contained 1:1 ratio of MTHF/water, as the concentration of 5-HMF increased, the concentration of LA also increased because of the equilibrium. As shown in Figure 4a-c, SEM images of the pinewood samples before and after the reaction showed remarkable variation in the surface morphology. In the reaction with MTHF/water solvent at 180 and 200 °C, the structure was completely disrupted and pores are created on the cell wall, whereas smooth surface can be seen in the untreated sample. These pores are clearly visible on both 180 and 200 °C treated residue samples and may suggest the extraction of lignin by contact with organic solvent following the reaction. Lignin is insoluble in water and soluble in MTHF and therefore can be separated by vacuum distillation. Lignin was recovered by this method from the reaction mixture as a semisolid material and tested by using FTIR spectra. The characteristic FTIR peak of lignin at 1515 nm (C-C aromatic stretching) was evident (Figure 5). However, as the boiling point of LA is high (245 °C) and it was difficult to separate it from the reaction mixture, some LA was recovered with lignin as seen in the peak at 1715 for the C=O group in LA.

The yield of desirable products from various feedstock was tested in 1:1 MTHF/water mixture at 180 °C (Table 5). The concentration of C₆ and C₅ sugars obtained from eucalyptus sawdust was less than that from pinewood after 15 min reaction time. The SEM images in Figure 4 also evidenced that the surface of the eucalyptus was partially damaged compared to that of pinewood. However, the concentration of FAL from eucalyptus sawdust was significantly higher than from pinewood. This may be caused by the presence of larger composition of C₅ carbohydrates, in particular, xylose. Typically, eucalyptus contains 15–17 wt% hemicellulose, 38–49 wt% cellulose and 28–31 wt% lignin^[22] in comparison to pinewood, which con-



Figure 4. a) Pinewood before treatment, b) after treatment at 180 °C c) after treatment at 200 °C, d) eucalyptus before treatment, e) after treatment at 180 °C. Reaction conditions: feedstock = 0.4 g, solvent (MTHF/water, w/w) = 20 g, LA = 0.1 g, reaction time = 15 min.



Figure 5. FTIR spectra of lignin byproduct obtained at a) 180 and b) 200 °C reaction temperature. 1) C=O group stretching in carboxylic acid; 2) C–C stretching in aromatic group.

Table 5. Conversion of different feedstock to chemicals. ^[a]									
Feedstock Concentration [mg L ⁻¹] C-ol H-ol 5-HMF FAL LA									
pinewood eucalyptus cellulose ^(b) glucose	2196 491 3410 1258	3090 2720 459 –	307 93 555 1570	288 565 106 –	177 - 80 175	40.7 37.0 24.3 20.0			
[a] Reaction condition: Feedstock = 0.4 g, solvent (MTHF/water, 1:1 w/w) = 20 g, LA catalyst = 0.1 g, reaction temperature = 180° C, reaction time = 15 min. [b] Reaction time = 1 h. Cello-oligomers (C-ol) = cellopentose + cellotettrose + cellotriose + cellobiose + glucose; hemi-monomers (H-ol) = xylose + arabinose + mannose.									

tains 20.6 wt% hemicellulose, 41.7 wt% cellulose and 25.9 wt% lignin.^[22b,23] Eucalyptus hemicellulose contains glucuronoxylan, xylan and acetyl groups, whereas pinewood hemicellulose contains galactoglucomannans, mannose and galactose units.^[22b,24] Concentration of C₆ sugars obtained from microcrystalline cellulose was three times higher than from pinewood sawdust after 60 min reaction, however, the dehydration into 5-HMF was comparatively lower. High sugar yield is expected from microcrystalline cellulose because the mass of the feedstock used was same as from eucalyptus sawdust; CHEMCATCHEM Full Papers

however, the latter sample contains only approximately $45\,\%$ cellulose.

Moreover, owing to the recalcitrance of crystalline cellulose depolymerisation reaction is the rate limiting step and longer times might be needed to achieve similar yield of 5-HMF. If using 0.4 g of glucose as a feedstock, 5-HMF was obtained as the major product (1570 mg L^{-1}) with a small quantity of LA byproduct. Only 20% of glucose was converted into 5-HMF and LA within 15 min reaction time at 180°C compared to 40.7% and 37% conversion of pinewood and eucalyptus sawdust. These results are comparable with those reported in literature.^[8,9f] Even though the reaction conditions are slightly different from those in the literature, the amount of glucose converted into 5-HMF is higher in the present case. In addition, Zhao et al. also reported that more than 70% yield of 5-HMF was obtained from glucose in the presence of 1-ethyl-3-methylimidazolium chloride [EMIM]Cl as a solvent with CrCl₂ salt.^[25] They proposed a mechanism with the plausible formation of CrCl₃⁻ from [EMIM]Cl and, further, that anions(CrCl₃⁻) play a role in proton transfer that could facilitating mutarotation of glucose in [EMIM], which results in fructose. In the present condition, LA catalyst may act as both Lewis acid and dehydrating agent. LA catalyst contains a carboxylic group at one end and a carbonyl group located in between the active methylene (CH₂) and the methyl group (CH₃). The carboxylate and carbonyl groups favour the formation of hydrogen bonds with the C₂-hydroxyl group of the glucose molecule, which facilitates keto-enol isomerisation. The carboxylic group can donate a proton that acts like a Brønsted site, which facilitates dehydration reaction. Recently, Luterbacher et al. reported high yields of carbohydrate production from hard and softwood biomass-derived $\gamma\text{-valerolactone}$ with a water co-solvent system with using dilute $\mathsf{H}_2\mathsf{SO}_4$ as a catalyst. $^{[1f]}$ Although the final concentrations of C₆ and C₅ sugars are low in the present work, it achieved better yields and selectivity of 5-HMF. The presence of the furan ring in MTHF, 5-HMF and FAL may facilitate the extraction and these reactive intermediates are highly stable in the organic phase.^[26] More importantly, MTHF is more volatile than FAL and 5-HMF, therefore separation of these products is easier by vacuum distillation process.^[19,27] Further the LA and lignin content in the organic phase can be separated by adding water to it. In addition by optimisation of reaction time, volume and temperature to maximise the yields from biomass conversion, the ratio of MTHF/water biphasic system allowed the additional control of the extent of reaction to achieve high yields of desirable products with good selectivity.^[28] Moreover, in this work the salts and mineral acid were replaced with LA, which along with MTHF can be produced from lignocellulose.

Conclusions

Levulinic acid (LA) was used as a catalyst for the conversion of lignocellulose biomass into 5-hydroxymethylfurfural (5-HMF) and furfural (FAL) in mono- and biphasic systems. LA showed several important benefits as the catalyst. LA is miscible in both water and MTHF solvents, therefore, it was equally parti-



tioned into the two phases. In the aqueous phase it depolymerised lignocellulose biomass followed by dehydration of sugar monomers to produce 5-HMF and FAL. The presence of LA in the aqueous phase maintained the equilibrium towards 5-HMF by preventing rehydration of 5-HMF into LA. Large fractions of 5-HMF and FAL were recovered in the MTHF phase, which is important for increasing the conversion of lignocellulose into these products and would allow easier separation downstream. Both hydrolysis and dehydration reactions were accelerated in the MTHF/water biphasic system compared to those in the pure aqueous system. Highest yields of 5-HMF and FAL were achieved with 1:1 w/w ratio of MTHF/water in a stirred reactor. Although highest conversion was achieved at 200 °C, the optimum temperature was found to be 180 °C at which good yield and higher selectivity of 5-HMF and FAL was achieved. Pinewood sawdust was found to yield higher amounts of desirable products than eucalyptus sawdust. The SEM micrographs showed clear indications of loss of material in the treated pinewood sample, compared to the treated eucalyptus samples.

Experimental Section

Materials

The following feedstock were used in this study: *pinus radiata* (pinewood, 550 μ m) and eucalyptus regnans (500 μ m) were obtained from Pollard's Sawdust Supplies, Victoria, Australia and Sigmacell microcrystalline cellulose (20 μ m) and D-glucose were obtained from Sigma-Aldrich.

Reaction procedure

The required amount (400 mg) of feedstock was taken into a 100 mL stainless-steel non-stirred Parr reactor and then LA (0.1 g, Aldrich 98%) as a catalyst was added followed by the solvent (20 g). MTHF (Sigma-Aldrich 99%), toluene (Sigma-Aldrich, 99%), and distilled water were used to make the mixture of MTHF/water (4:1, 2:1, 1:1, 1:2 and 1:4 w/w ratio) and toluene/water (1:1 w/w ratio) that were used as solvents in this reaction. The reactor was initially purged with N₂ to flush out air and then pressurized with nitrogen gas up to 10 bar. The reactor was heated to the desired temperature (140 to 200 °C) as measured by internal thermocouple and the reaction was conducted for time periods between 15 and 120 min. After the reaction, the unreacted solid was filtered from the reaction mixture, dried at 85 °C for 24 h and weighed. The organic phase was separated from the aqueous phase by using a separating funnel. Reactions were also conducted in a 300 mL Berghof stirred reactor at a stirring speed of 400 rpm containing pinewood sawdust (1 g), LA (0.25 g) and the solvent mixture (50 g). Mass conversion was calculated according to the following equation:

Mass Conversion, X (%) =
$$\left(1 - \frac{\text{Mass of unreacted solid}}{\text{Mass of feed solid}}\right) \times 100$$
(1)

Molar yield of 5-HMF was calculated according to the following equation:

Yield of 5-HMF (%) =

$$\left(\frac{\text{Moles of 5-HMF}}{\text{Theoretical moles of glucose in the feed}}\right) \times 100$$
⁽²⁾

The theoretical moles of glucose are based on 41.7 wt% cellulose content in *p. radiata*.^[17]

The distribution of 5-HMF and FAL in the organic phase was calculated according to the following equations:

Distribution of 5-HMF in organic phase
$$(\%) =$$

$$\left(\frac{\text{Mass of 5-HMF in organic phase}}{\text{Total mass of 5-HMF in the product}}\right) = \times 100$$
(3)

Distribution of FAL in organic phase (%) =

$$\left(\frac{\text{Mass of FAL in organic phase}}{\text{Total mass of FAL in the product}}\right) \times 100$$
⁽⁴⁾

By definition, the distribution of 5-HMF and FAL in the aqueous phase will be 100 minus the distribution in the organic phase.

Product analysis

After each experiment, both aqueous and organic phases were sampled and analysed by using HPLC equipped with Rezex RHM-Monosacccharide 300×7.80 mm column. Retention times and quantitation of sugars, HMF, LA and FAL were undertaken by comparison of retention times and calibration curves derived from peak areas of pure standards. Surface morphology of the pine-wood and eucalyptus sawdust samples before and after the reaction were analysed using FEI Magellan 400 FEGSEM scanning electron microscope (SEM). Lignin byproduct was characterized using a PerkinElmer Spectrum GX FTIR with spectral resolution of 4 cm⁻¹. The spectrum represents an average of 10 scans.

Acknowledgements

The authors acknowledge the funding from CSIRO Flagship Collaboration Fund. The authors thank Ms Kathryn Waldron, Monash Centre for Electron Microscopy, for her help with the SEM analysis.

Keywords: acidity • biomass • biphasic catalysis carbohydrates • hydrolysis

- a) D. M. Alonso, J. Q. Bond, J. A. Dumesic, Green Chem. 2010, 12, 1493– 1513; b) F. L. Chan, A. Tanksale, ChemCatChem 2014, 6, 2727–2739; c) F. L. Chan, K. Umeki, A. Tanksale, ChemCatChem 2015, 7, 1329–1337; d) M. J. Climent, A. Corma, S. Iborra, Green Chem. 2011, 13, 520–540; e) G. W. Huber, S. Iborra, A. Corma, Chem. Rev. 2006, 106, 4044–4098; f) J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger, J. A. Dumesic, Science 2014, 343, 277–280; g) L. R. Lynd, J. H. Cushman, R. J. Nichols, C. E. Wyman, Science 1991, 251, 1318–1323.
- [2] a) N. R. Savadekar, S. T. Mhaske, Carbohydr. Polym. 2012, 89, 146–151;
 b) V. K. Thakur, M. K. Thakur, Carbohydr. Polym. 2014, 109, 102–117.
- [3] C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning, K. Egeblad, ChemSusChem 2008, 1, 283–289.
- [4] a) M. Bicker, D. Kaiser, L. Ott, H. Vogel, J. Supercrit. Fluids 2005, 36, 118–126; b) A. Shrotri, L. K. Lambert, A. Tanksale, J. Beltramini, Green Chem. 2013, 15, 2761–2768; c) S. Dutta, S. De, B. Saha, ChemPlusChem 2012, 77, 259–272.



- [5] a) H. Ait Rass, N. Essayem, M. Besson, Green Chem. 2013, 15, 2240–2251; b) Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, Nature 2007, 447, 982–U985; c) Y. Román-Leshkov, J. A. Dumesic, Top. Catal. 2009, 52, 297–303.
- [6] S. Bhogeswararao, D. Srinivas, J. Catal. 2015, 327, 65-77.
- [7] G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, Science 2005, 308, 1446–1450.
- [8] Y. J. Pagán-Torres, T. F. Wang, J. M. R. Gallo, B. H. Shanks, J. A. Dumesic, ACS Catal. 2012, 2, 930–934.
- [9] a) J. B. Binder, R. T. Raines, J. Am. Chem. Soc. 2009, 131, 1979–1985;
 b) R. L. Huang, W. Qi, R. X. Su, Z. M. He, Chem. Commun. 2010, 46, 1115–1117;
 c) A. Takagaki, M. Ohara, S. Nishimura, K. Ebitani, Chem. Commun. 2009, 6276–6278;
 d) M. Von Sivers, G. Zacchi, Bioresour. Technol. 1995, 51, 43–52;
 e) H. P. Yan, Y. Yang, D. M. Tong, X. Xiang, C. W. Hu, Catal. Commun. 2009, 10, 1558–1563;
 f) Y. Yang, C. W. Hu, M. M. Abu-Omar, Green Chem. 2012, 14, 509–513.
- [10] a) J. B. Binder, R. T. Raines, *Proc. Natl. Acad. Sci. USA* 2010, *107*, 4516–4521; b) K. Shill, S. Padmanabhan, Q. Xin, J. M. Prausnitz, D. S. Clark, H. W. Blanch, *Biotechnol. Bioeng.* 2011, *108*, 511–520.
- [11] L. C. Peng, L. Lin, J. H. Zhang, J. P. Zhuang, B. X. Zhang, Y. Gong, *Molecules* 2010, 15, 5258–5272.
- [12] B. R. Caes, R. T. Raines, ChemSusChem 2011, 4, 353-356.
- [13] Y. Simeó, J. V. Sinisterraa, A. R. Alcantara, Green Chem. 2009, 11, 855– 862.
- [14] a) D. F. Aycock, Org. Process Res. Dev. 2007, 11, 156–159; b) S. Shanmu-ganathan, L. Greiner, P. D. de Maria, Tetrahedron Lett. 2010, 51, 6670–6672; c) H. Yang, S. Mahapatra, P. H. Y. Cheong, R. G. Carter, J. Org. Chem. 2010, 75, 7279–7290.
- [15] V. Pace, P. Hoyos, L. Castoldi, P. D. de Maria, A. R. Alcantara, *ChemSus-Chem* 2012, *5*, 1369–1379.
- [16] J. G. Lynam, C. J. Coronella, W. Yan, M. T. Reza, V. R. Vasquez, *Bioresour. Technol.* 2011, *102*, 6192–6199.
- [17] NREL, U.S. Department of Energy; http://www.nrel.gov/biomass/data_ resources.html.

- [18] a) Y. Yang, C. W. Hu, M. M. Abu-Omar, *ChemSusChem* 2012, *5*, 405–410;
 b) F. S. Asghari, H. Yoshida, *Carbohydr. Res.* 2010, *345*, 124–131; c) Z. H. Zhang, Z. B. K. Zhao, *Bioresour. Technol.* 2010, *101*, 1111–1114.
- [19] R. Weingarten, A. Rodriguez-Beuerman, F. Cao, J. S. Luterbacher, D. M. Alonso, J. A. Dumesic, G. W. Huber, *ChemCatChem* 2014, 6, 2229–2234.
- [20] a) C. M. Cai, T. Y. Zhang, R. Kumar, C. E. Wyman, *Green Chem.* 2013, *15*, 3140–3145; b) J. P. Lange, E. van der Heide, J. van Buijtenen, R. Price, *ChemSusChem* 2012, *5*, 150–166.
- [21] X. Hu, L. P. Wu, Y. Wang, Y. Song, D. Mourant, R. Gunawan, M. Gholizadeh, C. Z. Li, *Bioresour. Technol.* **2013**, *133*, 469–474.
- [22] a) R. P. KibbleWhite, M. J. C. Riddell, C. J. A. Shelbourne, *New Zealand J. Forestry Sci.* 2000, *30*, 458–474; b) R. F. H. Dekker, *Biocatal. Biotransform.* 1987, *1*, 63–75; c) M. Brink, E. G. Achigan-Dako, *Fibres*, PROTA Foundation, 2012.
- [23] a) A. Ferraz, J. Baeza, J. Rodriguez, J. Freer, *Bioresour. Technol.* 2000, *74*, 201–212; b) K. K. Y. Wong, K. F. Deverell, K. L. Mackie, T. A. Clark, L. A. Donaldson, *Biotechnol. Bioeng.* 1988, *31*, 447–456.
- [24] a) G. Koch in *Handbook of Pulp*, Wiley-VCH, Weinheim, 2008, pp. 21–68;
 b) M. G. Grønli, G. Várhegyi, C. Di Blasi, *Ind. Eng. Chem. Res.* 2002, *41*, 4201–4208; c) T. E. Timell, *Wood Sci. Technol.* 1967, *1*, 45–70; d) P. Reyes, R. T. Mendonça, J. Rodríguez, P. Fardim, B. Vega, *J. Chil. Chem. Soc.* 2013, *58*, 1614–1618; e) C. Stewart, D. Foster, *Aust. J. Chem.* 1953, *6*, 431–438.
- [25] H. B. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, Science 2007, 316, 1597–1600.
- [26] X. Hu, R. J. M. Westerhof, D. H. Dong, L. P. Wu, C. Z. Li, ACS Sustainable Chem. Eng. 2014, 2, 2562–2575.
- [27] J. N. Chheda, Y. Román-Leshkov, J. A. Dumesic, Green Chem. 2007, 9, 342–350.
- [28] C. M. Cai, N. Nagane, R. Kumar, C. E. Wyman, Green Chem. 2014, 16, 3819–3829.

Received: October 8, 2015 Revised: November 10, 2015 Published online on December 8, 2015