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The breakdown of reticent biomass to soluble components and their conversion to levulinic acid as a fuel precursor†

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A biphasic system consisting of THF and water was studied to achieve the integrated conversion of cellulose and hemicellulose in lignocellulosic biomass to levulinic acid. As compared to previous studies using GVL as solvent, the utilization of a lower boiling point solvent, THF, also achieves the simultaneous hydrolysis of C_6 and C_5 carbohydrates in lignocellulosic biomass, and the results of simultaneous hydrolysis are comparable. Furthermore, it offers an alternative operation procedure after the hydrolysis. A distillation process is not only used to achieve the effective separation of the solid residue from the desired products, but it also helps in the complete isolation of furfural and formic acid from levulinic acid. Consequently, the utilization of by-product formic acid in the hydrogenation of furfural to furfuryl alcohol is explored, and the process is achieved with both model substrates and the feed from the lignocellulosic biomass feedstock. The hydrolysis of furfuryl alcohol gave C_5 carbohydrate-derived levulinic acid. We finally explored the integrated conversion with five biomass raw materials, and the total yield of levulinic acid was quite obviously promoted by the additional conversion of pentose.

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1. Introduction

With the rapid decline of fossil fuel reserves, a growing number of researchers have started to study the use of lignocellulosic biomass to replace petroleum and to produce chemicals and liquid fuels.[1,2] Lignocellulosic biomass is mainly composed of three components, cellulose, hemicellulose and lignin. Cellulose and hemicellulose can be converted to ethanol, 5-hydroxymethylfurfural (HMF),[3] 2,5-dimethylfuran (DMF),[4] levulinic acid and methyl furan,[5] along with other energy platform molecules. Levulinic acid, as one of twelve top sugar-derived building blocks, can be converted to fuel additives such as γ-valerolactone (GVL)[6–8] and valeric esters.[9] Furthermore, levulinic acid-derived GVL can be converted to liquid alkenes in the transportation fuel range.[10] Thus, levulinic acid is considered as a chemical bridge to connect biomass and petroleum.[11]

In the literature, the direct hydrolysis of biomass-derived C_6 carbohydrates into levulinic acid has been studied as the main pathway for generating levulinic acid from biomass, with 5-hydroxymethylfurfural as the intermediate.[12] In this process, the dehydration of C_6 sugars such as glucose, starch or cellulose is achieved with Brønsted acid or solid acid catalysts.[13] The reaction media could be water, organic solvent or a mixed solvent system consisting of biomass-derived solvent and water.[14] However, the content of C_6 carbohydrates in natural lignocellulosic biomass is no more than 55 wt%.[15] If levulinic acid was only produced from C_6 carbohydrates, the energy efficiency would be only 22.0% in this levulinic acid-based biomass to biofuel strategy.[16] Recently, an integrated conversion of both C_6 and C_5 carbohydrates in biomass to levulinic acid was reported by Dumesic *et al.*[17] The reaction was conducted in a mixed solvent of biomass-derived GVL and water. The hydrolysis of C_5 carbohydrates to furfural and C_6 carbohydrates to levulinic acid occurred simultaneously. Then furfural was hydrogenated to furfuryl alcohol, which was finally hydrolyzed to levulinic acid. The additional conversion of C_5 carbohydrates to levulinic acid effectively improved the carbon utilization and energy efficiency in the levulinic acid-based biomass to biofuel strategy, and the solvent system consisting of GVL and water was the key issue in this work. We proposed that more solvent systems should be studied to further explore the advantages in the integrated conversion.

Herein, we report the integrated conversion of both C_6 and C_5 carbohydrates in lignocellulosic biomass to levulinic acid in a biphasic system consisting of THF and water. THF could be considered as a biomass-derived solvent, and it could be produced from furfural by the combination of decarbonylation and ring hydrogenation.[18] Furthermore, the biphasic system of THF and water has been used in many biomass conversion processes, such as the dehydration of hexose and pentose to HMF and furfural, respectively.[19] Based on these previous works, we explored the integrated conversion of both C_6 and C_5

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carbohydrates to levulinic acid in the biphasic system of THF and water for the first time. As shown in Scheme 1, C_6 and C_5 carbohydrates in biomass were first hydrolyzed in one step to levulinic acid + formic acid and furfural, respectively. This hydrolysis process was firstly investigated with model substrates, then with raw biomass materials, and the results were comparable to values observed in the solvent system of GVL and water. However, as compared to GVL, the lower boiling point of THF (66 °C) allowed the product solution to be easily separated into three fractions by one-step distillation. Lignin and humins were precipitated as a solid residue. At the same time, furfural, formic acid, water and THF were isolated in the gaseous fraction, and levulinic acid, catalyst acid, and a little water remained in the liquid fraction. There are two advantages of our separation step. Firstly, it was easy to operate and the solid residue could be isolated from the desired product effectively. Secondly, after the complete isolation of furfural and formic acid from levulinic acid, we could explore the utilization of by-product formic acid in the hydrogenation of furfural to furfuryl alcohol without any interference. We initially investigated the model hydrogenation of furfural with formic acid, and then the hydrogenation of a feed from lignocellulosic biomass was also achieved. Furfuryl alcohol was finally hydrolyzed to give C_5 carbohydrates-derived levulinic acid, and the total yield of levulinic acid was quite obviously promoted by the additional conversion of pentose. Five biomass raw materials were investigated in our process, and the highest mass yield of levulinic acid that could be attained was 27.7 wt% with the conversion of corn cob.

2. Experimental

2.1 Materials and analysis

2.1.1 List of chemicals. Xylan from birch wood (xylose residue >90%, Sigma-Aldrich), cellulose (Alfa Aesar), levulinic acid (99%, Aladdin Reagent Co. Ltd.), hydrochloric acid, formic acid, sodium chloride, furfural, glucose and xylose (Sinopharm Chemical Reagent Co. Ltd.), furfuryl alcohol (98%, Aladdin Reagent Co. Ltd.). THF was purchased from Sinopharm Chemical Reagent Co. Ltd., and anhydrous THF was obtained by refluxing THF with sodium. The anhydrous THF was used when studying the effect of water content in the solvent.

The biomass feedstocks used in this work were collected from Hefei in China. Each biomass feedstock was air-dried, crushed, screened to select the fraction of particles with a size less than 0.3 mm. The dilute acid pretreatment was not conducted in the conversion of biomass feedstocks. We carried out experiments to check the feedstock compositions and we quoted the prices of biomass feedstocks which were reported by Dumesic *et al.*[16a] (see Table 1).

2.1.2 Analysis

(a) Analysis of the liquid product. The quantitative analysis of levulinic acid and formic acid was performed on a Waters 1515 series HPLC (250*4.6 Agilent HC-C18 column) with a RI detector using a 5 mM aqueous sulfuric acid solution as eluent. The total yield of levulinic acid in the biphasic system was calculated by the yield of levulinic acid in the water phase plus the yield in the organic phase. To determine the yields, the solution was diluted 10 times in water, and then transferred to the HPLC.

The concentration of furfural was detected by HPLC using the external standard method. HPLC was performed on a Hitachi L-2000 HPLC system equipped with two L-2130 pumps and an L-2455 photodiode array detector. Furfural was analyzed by reversed-phase chromatography on an Alltech C18 packed column (250 × 4.6 mm, Alltech) at a column temperature of 30 °C. The flow of the mobile phase was methanol and water (methanol–water = 20 : 80) at a flow rate of 1.0 ml min^{-1}. The detection wavelength of furfural was 277 nm. The total yield of furfural was also calculated by the yield of furfural in the water phase plus the yield in the organic phase.

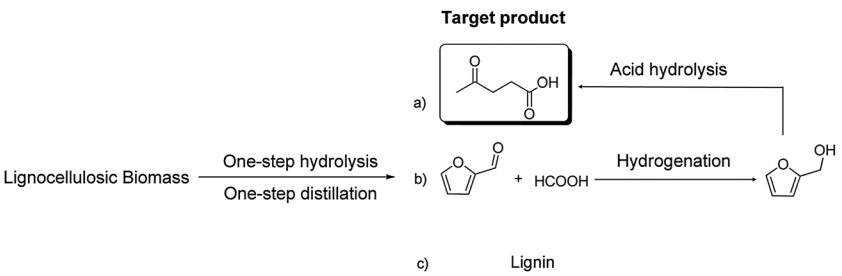
(b) Analysis of the water content. The analysis of the water content was performed on a Karl Fischer Moisture Titrator, and each sample was analyzed three times.

(c) Analysis of the solid product. After filtration, the solid residue was collected and dried at 60 °C in air. The solid residue was weighed and its SEM image is shown in Fig. S2.†

(d) Calculation of the products. The yields of furfural and levulinic acid in the model hydrolysis were defined as follows:

$$\text{Yield} = (\text{moles of furfural/levulinic acid produced})/(\text{moles of sugar units in initial xylan/cellulose}) \times 100\%$$

All the yields of furfural and levulinic acid after the hydrolysis of lignocellulosic biomass were detected after the distillation, and they were defined as follows. The weight of hemicellulose was considered as the weight of total pentose, and the weight of cellulose was considered as the weight of total hexose.



Scheme 1 Illustration of the integrated conversion of C_6 carbohydrates and C_5 carbohydrates in lignocellulosic biomass to levulinic acid in a biphasic solvent system consisting of THF and water.

Table 1 Compositions (in wt%) and prices of biomass feedstocks used in our research

	Corn stover	Bagasse	Poplar	Pine	Corn cob
Cellulose	36.00	41.27	48.15	52.82	36.21
Hemicellulose	21.36	21.91	17.25	10.6	37.16
Lignin	18.67	17.32	27.17	29.50	7.05
Others	23.97	19.5	7.43	7.7	19.58
Total	100	100	100	100	100
Price[16a] $ per dry ton	83.00	40.00	50.70	57.32	—

Molar yield of furfural = (weight of furfural after distillation)/(weight of hemicellulose in biomass raw material) × 132/96 × 100%

Molar yield of levulinic acid = (weight of levulinic acid after distillation)/(weight of cellulose in biomass raw material) × 162/116 × 100%

Mass yield = (weight of furfural/levulinic acid after distillation)/(weight of biomass raw material) × 100%

2.2 General procedure for detecting the composition of lignocellulosic biomass

From every crushed biomass feedstock at least 200 g was collected to ensure the composition of biomass feedstock was similar in each experiment. The composition of the lignocellulosic biomass used in our experiments was determined by the method reported in the literature,[20] and the results are listed in Table 1. The methods are based on the use of neutral and acid detergents for the removal of soluble carbohydrates, proteins and tannins. The neutral detergent fiber (NDF) method provides a measure of the total cell-wall material (cellulose, hemicellulose and lignin). In this test, a lignocellulosic biomass sample of known weight was autoclaved for 15 minutes at 121 °C in a neutral solution containing ethylene-diamine tetra acetate dihydrate, sodium borate decahydrate, sodium lauryl sulphate, 2-ethoxyethanol, disodium hydrogen phosphate, decahydronapthalene and sodium sulphite. Following this, the remaining solid was filtered, washed and then incubated with an amylase solution overnight at 37 °C. After incubation, the residue was washed with acetone and dried at 105 °C for 4 hours. The final residue was weighed. The NDF is the percent of the original material that is residue. The acid detergent fiber (ADF) method determines the cellulose plus lignin content and consequently, the difference between NDF and ADF provides a determination of hemicellulose. The ADF method involves the autoclaving of the sample in a solution of cetyltrimethylammonium bromide, sulphuric acid, and decahydronapthalene at 121 °C for 15 minutes. The residue is filtered, washed, rinsed with acetone and then dried at 105 °C for 4 hours. The ADF is the percentage of the original material that is residue. Lignin may be found separately in the ADF fraction by removal of lignin by permanganate oxidation. This is called the acid detergent lignin (ADL) method. The residue from the ADF method is digested with 72% sulphuric acid for 3 hours and then washed, dried and weighed. The sample is then ashed at 550 °C for 3 hours and then weighed again. The ADL is the change in weight during ashing as a percentage of the original straw sample. Hemicellulose content is found by the difference between NDF and ADF and the cellulose content is the difference between ADF and ADL.

Table 2 Model investigation of one-step acid hydrolysis of cellulose and xylan[a]

							Yield [mol%]	
Entry	T_1 [°C]	t_1 [min]	T_2 [°C]	t_2 [min]	NaCl [wt%]	$V_{org.}/V_{aq.}$	Levulinic acid[d]	Furfural[e]
1	110	40	200	20	—	0	47.3	0
2	110	40	200	20	5	2 : 1	53.8(1.625)	42.0(2.735)
3	110	40	200	20	10	2 : 1	58.8(2.885)	58.6(5.493)
4	110	40	200	20	20	2 : 1	48.5(4.865)	59.2(11.19)
5	110	40	200	20	30	2 : 1	47.2(7.13)	65.1(27.36)
6	—	—	200	20	10	2 : 1	57.0	47.5
7	110	40	200	10	10	2 : 1	47.1	52.5
8	110	40	200	40	10	2 : 1	53.8	44.1
9	110	40	220	20	10	2 : 1	49.1	37.8
10	110	40	180	20	10	2 : 1	46.0	46.6
11[b]	110	40	200	20	10	2 : 1	44.2	52.7
12	110	40	200	20	10	1 : 1	51.5	26.5
13[c]	110	40	200	20	10	2 : 1	45.4	59.0

[a] Reaction conditions: 2 g cellulose, 1 g xylan, a 0.8 M hydrochloric acid solution and THF (water + THF = 60 ml), were stirred in a 150 ml autoclave made of zirconium alloy. [b] Use of 0.4 M HCl. [c] Use of 0.8 M H_2SO_4. [d] The value in parentheses is the partition coefficient of HMF. [e] The value in parentheses is the partition coefficient of furfural.

Table 3 Investigation of one-step acid hydrolysis of lignocellulosic biomass[a]

Entry	Substrate	HCl [M]	T_1 [°C]	t_1 [min]	T_2 [°C]	t_2 [min]	NaCl [wt%]	$V_{org.}/V_{aq.}$	Yield [mol%] Levulinic acid	Yield [mol%] Furfural
1	Xylose[b]	0.8	—	—	200	20	10	2 : 1	—	76.9
2	Bagasse	0.4	110	40	200	20	10	2 : 1	58.5	40.1
3	Bagasse	0.4	110	40	200	20	10	2 : 1	44.3	66.3
4	Bagasse	0.4	110	40	210	20	10	2 : 1	55.6	60.9

[a] Reaction conditions: 4 g bagasse, a hydrochloric acid solution and THF (water + THF = 60 mL), was stirred in a 150 mL autoclave made of zirconium alloy. [b] The substrate is 1 g xylose.

2.3 General procedure for model reactions

2.3.1 Model hydrolysis. For typical runs, cellulose (2 g), xylan (1 g) and NaCl (mass depends on the reaction condition) was loaded in a 150 ml Zr alloy autoclave, then a hydrochloric acid aqueous solution (20 ml) and THF (40 ml) were added to the autoclave. The autoclave was flushed with nitrogen, and the pressure of the remaining nitrogen was 0.5 MPa. The autoclave was stirred at 850 rpm, and the temperature of the autoclave was elevated to the target temperature in 35 min. After the completion of reaction, the autoclave was cooled to room temperature with ice. The yields of levulinic acid and furfural were determined by HPLC.

2.3.2 Model distillation. For model distillation, levulinic acid (1 g), furfural (0.5 g), formic acid (0.5 g) were added into a solvent system consisting of water (20 ml) and THF (40 ml). The weights of these chemicals were close to the values in the product solution after the hydrolysis of lignocellulosic biomass. During the distillation, furfural and formic acid were easily removed with THF and water, and then they were collected in a cold trap. Levulinic acid was kept in the solution. Furfural and formic acid could be removed completely with distillation at 50 °C, leaving less than 1% furfural and formic acid in the solution.

2.3.3 Model hydrogenation of furfural with formic acid. The model hydrogenation was carried out to determine the optimum hydrogenation conditions (Table 3). All the catalytic experiments were carried out in a 50 ml Parr autoclave made of zirconium alloy. Furfural, formic acid, catalyst and solvent were firstly added to the autoclave. Then N_2 was used to exclude the air. The mixture of substrates and catalyst was heated to the desired temperature in 20 min with vigorous stirring.

2.4 General procedure for integrated conversion of lignocellulosic biomass in the biphasic system

The integrated conversion of lignocellulosic biomass to levulinic acid in our research contained four main steps.

2.4.1 One-step hydrolysis of lignocellulosic biomass to levulinic acid and furfural. For typical runs, lignocellulosic biomass feedstock (4 g), NaCl (2 g), 0.4 M hydrochloric acid aqueous solution (20 ml), and THF (40 ml) were added to a 150 ml Zr alloy autoclave. Then the autoclave was flushed with nitrogen, and the pressure of the remaining nitrogen was 0.5 MPa. The autoclave was stirred at 850 rpm, and the temperature of the autoclave was elevated to the target temperature in 35 min. After the reaction was finished, the autoclave was cooled to room temperature with ice. The product solution was transferred to the distillation step.

2.4.2 One-step distillation of the product solution. The operation of the distillation of the solution after the hydrolysis of the lignocellulosic biomass was the same as the model distillation. Furfural and formic acid could be removed with THF and water during the distillation, while lignin and humins were precipitated simultaneously to be easily isolated from the levulinic acid solution by filtration. The solution of furfural and formic acid was further converted to levulinic acid solution.

2.4.3 Conversion of furfural and formic acid to furfuryl alcohol. The optimum solvent in the model hydrogenation was the mixture of water and THF (1 : 19). However, after distillation, the water content in the gaseous fraction was much higher than this value. An extraction process was needed to decrease the water content. For the extraction operation, NaCl (the ratio of it to biomass feedstock was 2 : 3) was firstly added to the distilled solution to saturate the water phase. Then the water phase was further extracted twice, so that the water content in the extracted organic phase was just 5% (detected by Karl Fischer Moisture Titrator). Furfural was extracted completely into the organic phase, and the extraction efficiency of formic acid was about 60%. After the adjustment of the water content, additional formic acid was added to achieve a 1 : 2 molar ratio of furfural to formic acid. Then the hydrogenation of furfural by formic acid was carried out and the reaction conditions were similar to the model hydrogenation.

2.4.4 Hydrolysis of furfuryl alcohol to levulinic acid. The hydrolysis of furfuryl alcohol to levulinic acid could be easily achieved by refluxing furfuryl alcohol with hydrochloric acid in a mixed solvent of THF and water, and the yield of levulinic acid was about 80%.

While mixing the furfuryl alcohol solution from step c and the levulinic acid aqueous solution from step b, the hydrolysis of furfuryl alcohol occurred with heating. The supplement of catalyst hydrochloric acid was needed because some hydrochloric acid was removed out in the distillation step, and the levulinic acid yield attained could reach 75% in this step.

The experiment to obtain the total yield of levulinic acid was carried out on a smaller-scale (1 g biomass feedstock), otherwise the solution volume in the hydrogenation of furfural will exceed 100 ml which cannot be operated in our autoclave at the time.

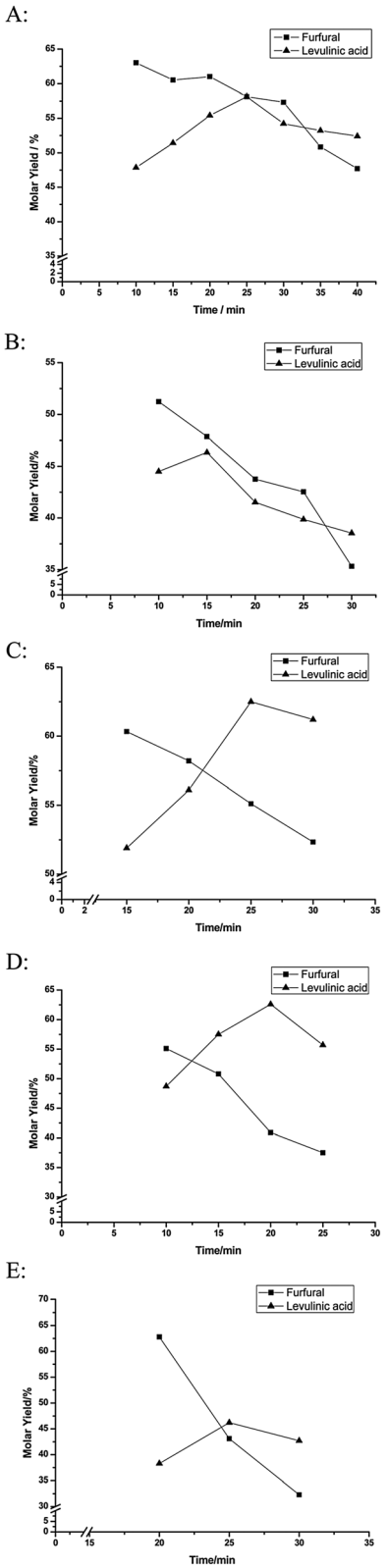


Fig. 1 The yields of furfural and levulinic acid after the one-step hydrolysis of baggase (A), poplar (B), corn cob (C), corn stover (D) and pine (E). Reaction conditions: 4 g biomass raw material, 20 ml aqueous solution (10 wt% NaCl and 0.4 M HCl), 40 ml THF. $T_1 = 110$ °C, $T_2 = 210$ °C.

Table 4 The results of the hydrogenation of furfural to furfuryl alcohol with formic acid as the hydrogen source[a]

Entry	Additive	Catalyst	T [°C]	t [h]	Conversion [%]	Yield [%]	Selectivity [%]
1	—	Pd/C	90	6	60.2	19.1	31.7
2	—	Ru/C	90	6	11.9	0.4	3
3	NaOH	Pd/C	90	6	65.8	8.3	12.7
4	NaOH	Ru/C	90	6	70.8	47.9	67.6
5[b]	NaOH	Ru/C	90	6	99.3	99.3	100
6[c]	NaOH	Ru/C	90	6	99.8	79.3	79.5
7[c]	NaOH	Ru/C	90	8	99.5	94.3	94.7
8[d]	NaOH	Ru/C	90	6	74.1	69.4	93.6
9[d]	NaOH	Ru/C	110	6	99.2	96.6	97.4
10[e]	NaOH	Ru/C	110	6	56.4	42.1	75.7
11[f]	NaOH	Ru/C	110	6	99.5	99.0	99.5

[a] Typical reaction conditions: furfural (2 mmol), FA (8 mmol), THF (20 ml), Pd/C or Ru/C (0.4 g), additive was 10 mol% to the formic acid. [b] Change the solvent to 19 ml THF and 1 ml H_2O. [c] Furfural (10 mmol), FA (40 mmol). [d] Furfural (2 mmol), FA (4 mmol). [e] Furfural (2 mmol), FA (2 mmol). [f] Feed from 1 g biomass raw material, additional 0.5 mmol formic acid was supplemented.

3. Results and discussions

3.1 Model acidic hydrolysis in the biphasic system

We firstly studied the acidic hydrolysis of biomass-derived carbohydrates. The simultaneous hydrolysis of C_6 and C_5 carbohydrates in a mixed solvent system of GVL and water has been reported recently. In our research, we firstly carried out the model hydrolysis of cellulose and xylan (mass ratio was 2 : 1, similar to the mass ratio in the lignocellulosic biomass) to check the occurrence of one-step hydrolysis in our biphasic system.

Initially, when water was used as the solvent, no furfural was detected while the yield of levulinic acid achieved 47.3% (Table 2, entry 1). The absence of furfural was most likely due to its reduced stability. In the literature, the hydrolysis of pentose usually occurs under milder reaction conditions (lower reaction temperature and lower acid concentration), and furfural was less stable in high reaction temperature.[21] When the reaction conditions were suitable for the generation of levulinic acid, all the furfural was condensed to humins. Some previous investigations have shown that biphasic systems consisting of organic solvent and water can effectively stabilize HMF and furfural, thereby improving the selectivity of HMF and furfural from carbohydrates.[22] However, the simultaneous production of levulinic acid and furfural from C_6 and C_5 carbohydrates in biphasic systems have not yet been reported. As compared to other common organic solvents, THF showed the best combination of partition coefficient of HMF in biphasic systems and HMF selectivity.[19a] We proposed that THF could also stabilize furfural to improve the selectivity of furfural, so a biphasic system consisting of THF and water was chosen in our optimization process. The NaCl salt was added into the water phase to increase the partition coefficient of unstable furfural, and the effect of the amount of NaCl was studied (Table 1, entries 2–5). The yield of furfural increased with the increasing

Table 5 The results of the conversion of various lignocellulosic biomass feedstocks to levulinic acid[a]

Entry	Feedstock	Best reaction time during hydrolysis	Yield of levulinic acid from C_6 carbohydrates[b] [wt%]	Yield of levulinic acid from C_5 carbohydrates[c] [wt%]	Total yield of levulinic acid [wt%]	Mass yield of solid residue[d] [wt%]
1	Bagasse	25	17.2 (58.1)	9.1 (58.1)	26.1	23.8
2	Corn stover	15	16.1 (62.6)	7.8 (40.3)	23.9	24.1
3	Poplar	15	16.1 (46.4)	5.8 (54.9)	21.9	27.3
4	Pine	25	17.5 (46.2)	4.5 (42.3)	22.0	35.2
5	Corn cob	25	16.4 (63.2)	11.3 (54.9)	27.7	16.1

[a] All the operation processes for lignocellulosic biomass conversion were described in the Experimental section. [b] The value in parenthesis is the molar yield of levulinic acid from C_6 carbohydrate in the lignocellulosic biomass. [c] The value in parenthesis is the molar yield of furfural from C_5 carbohydrate in the lignocellulosic biomass. [d] The solid residue consisted of unreacted lignin and humins generated in the hydrolysis process.

concentration of NaCl. However, the tendency of the yield of levulinic acid was not the same as the furfural yield, and the highest yield of levulinic acid was observed with a NaCl content of 10 wt%. We found that the increase of NaCl content raised both the partition coefficient of furfural and HMF (the data was shown in Table 2). Therefore, the yield of furfural increased while more furfural was extracted to the organic phase. However, while more HMF was present in the organic phase, difficulties surrounding the contact of HMF with the acid catalyst in the water phase led to a decrease in the yield of levulinic acid. By considering both the yields of furfural and levulinic acid, we selected a NaCl content of 10 wt% as the optimized concentration of the salt. Both the yields of furfural and levulinic acid were nearly 60%. The reaction temperature also had a great impact on the hydrolysis yield. The hydrolysis should be performed at 110 °C for 40 minutes to achieve a higher yield of furfural. This was most likely due to a predepolymerization of xylan to xylose at this temperature (Table 2, entries 3 and 6). The best final hydrolysis temperature was 200 °C, and the optimized reaction time was 20 min (Table 2, entries 7–10). A decrease in the concentration of the acid and the mass ratio of the organic phase to water phase led to a reduction of the yields of the hydrolysis products (Table 2, entries 11 and 12). The use of sulphuric acid gave an obviously lower yield of levulinic acid. Overall, we demonstrated that the one-step hydrolysis of xylan and cellulose could also be achieve in the biphasic system, and the molar yield of levulinic acid was 58.8% while the furfural molar yield was 58.6%. These results were comparable to values observed in the solvent system of GVL and water.

3.2 Distillation of product solution

The results of the model hydrolysis of cellulose and xylan provided the possibility of the one-step hydrolysis of lignocellulosic biomass in the biphasic system. When we turned to study the hydrolysis of the lignocellulosic biomass, we found it was more complex than the model reaction because of its complex structure which comprised of cellulose, hemicellulose and lignin. In addition, though the unreacted lignin and the by-product humins dissolved very well in the organic phase after the hydrolysis process, they were precipitated immediately with the addition of water at the detection step, and the precision of the detection of the hydrolysis product was greatly interfered. Hence, before the investigation of the hydrolysis of lignocellulosic biomass, a simple and appropriate method was sought to isolate lignin and humins from the production solution which was also a necessary step in the process of lignocellulosic biomass conversion.

We noticed that both furfural and formic acid could form an azeotrope with water, and the boiling points were 97.5 °C and 107.3 °C, respectively. These boiling points were far below the boiling point of levulinic acid (b.p. = 246 °C), so we tried to separate the product solution by vacuum distillation at a low temperature. The model distillation of the mixture of levulinic acid, formic acid and furfural was firstly carried out, and more detailed conditions are shown in the Experimental section. During the distillation, furfural and formic acid were easily separated with THF and water, and levulinic acid remained in the solution. While the distillation temperature achieved 50 °C, furfural and formic acid could be removed completely from levulinic acid (less than 1% furfural and formic acid remained in the liquid fraction).

The distillation of the feed from the hydrolysis of lignocellulosic biomass was also carried out, and bagasse was firstly studied as the biomass feedstock in this section. Before the distillation, the weights of the hydrolysis products were detected, furfural (0.414 g), formic acid (0.412 g) and levulinic acid (0.635 g). It should be noted that in the detection step, due to the interference of solid residues, the detection results of the hydrolysis products varied over a large range (more than 10%) even with the same sample. The result we gave was just one of them. After distillation, the product solution was separated into three fractions at a distillation temperature below 50 °C. The gaseous fraction contained furfural (0.369 g), formic acid (0.444 g), THF and water. The liquid fraction contained levulinic acid (0.686 g) and the catalyst acid with less than 1% (about 0.5%) furfural and formic acid remaining, and the last solid fraction was the solid residue consisting of lignin and humans. The distillation process could be reproduced successfully. Though the detection of hydrolysis products before distillation is not precise due to interference, the comparison of these results partially demonstrated that the one-step distillation was also achieved with the feed from biomass raw materials. Overall, after the simultaneous hydrolysis, a one-step distillation not

only effectively separated lignin and humins from the desired products, but it also achieved the isolation of furfural and formic acid from levulinic acid.

3.3 One-step hydrolysis of biomass raw materials

The effective isolation of lignin and humins led to a feasible detection of the hydrolysis products from lignocellulosic biomass, and we started to optimize the reaction conditions during biomass hydrolysis. In this section, the detection of hydrolysis products was achieved after the distillation, and only acetic acid was observed as a by-product (less than 5 wt%). Bagasse was firstly used as a substrate. In contrast to the model hydrolysis, we found that a lower HCl concentration (0.4 M) and a higher reaction temperature (210 °C) were favourable for the hydrolysis of lignocellulosic biomass, and the results are listed in Table 3. Under the above reaction conditions, the yields of furfural and levulinic acid *versus* reaction time are shown in Fig. 1. The yield of furfural decreased with the increase of reaction time, but the yield of levulinic acid fluctuated with the reaction time. We choose 25 min as the best reaction time and both the molar yields of levulinic acid and furfural were about 58%. The molar yield of formic acid and levulinic acid were about 1.1 : 1 in the hydrolysis of C_6 carbohydrates, but in our research we found that the ratio of formic acid to levulinic acid was about 1.6 : 1. The extra portion of formic acid was most likely due to the hydrolysis of the formyl group in hemicellulose. The mass yield of the solid residue was 19.12 wt%. Finally, the hydrolysis conditions were further applied to the conversion of other lignocellulosic biomass feedstocks and the results were are shown in Fig. 1. These results demonstrated that lignocellulosic biomass could undergo one-step hydrolysis in the biphasic system.

3.4 Hydrogenation of furfural with formic acid

After the optimization of the hydrolysis reaction conditions, we started to study the conversion of furfural in the gaseous fraction (after distillation) to furfuryl alcohol through a Ru-catalyzed process. The gaseous fraction after distillation was a mixed solution of furfural, formic acid, THF and water, and the hydrogenation of furfural to furfuryl alcohol with formic acid as hydrogen source was investigated. A model hydrogenation was firstly studied, and a mixed solvent system of THF and water was used as the solvent (see Table 4). The hydrogenation of furfural with 4 equivalents formic acid was used to explore the optimized ratio of water to THF. While the ratio of water to THF was 1 : 19 (the effect of water content in the solution is shown in Fig. S1†), the 100% selectivity of furfuryl alcohol was achieved with 99.3% conversion of furfural, and 10 mol% NaOH was added in the solution (Table 4, entry 5). However, in our hydrolysis process, the molar ratio of formic acid and furfural in the hydrolysis solution was generally about 2 : 1, so the amount of formic acid was further reduced to 2 equivalents of furfural in the model hydrogenation. After optimizing the reaction conditions, we found that the selectivity of furfuryl alcohol could reach 97.4%, while the conversion of furfural was 99.2% (Table 4, entry 9). Further decreases in the amount of formic acid to 1 equivalent led to a decrease in both the conversion of furfural and the selectivity of furfuryl alcohol.

After the model hydrogenation, we studied the hydrogenation of furfural in the feed from lignocellulosic biomass conversion. In the model hydrogenation, the best solvent was a mixed solvent of THF and water (v/v = 19 : 1). However, after distillation, the water content in the gaseous fraction was higher than this value (nearly 20%). Therefore, the hydrogenation process was depressed, and both the conversion of furfural and the selectivity of furfuryl alcohol were very low. To solve this problem, an extra extraction operation was added before the hydrogenation process of the feed from biomass. After the extraction operation, furfural was completely extracted into the organic phase, and the water content was successfully decreased to 5%. However, the extraction efficiency of formic acid was not very good (about 60%), so a supplement of formic acid was needed. Our previous work had shown the possibility of the production of formic acid from biomass-based carbohydrates,[23] so the supplementary formic acid could also be considered as biomass-derived. Finally, the hydrogenation of the feed from biomass raw material was successfully achieved (Table 4, entry 11), the selectivity of furfuryl alcohol was 99.5% with a 99.5% conversion of furfural under the same reaction conditions as the model reaction. The reaction solution initially contained about 1 mmol furfural and 1.5 mmol formic acid, and an additional 0.5 mmol formic acid was supplemented. This hydrogenation process was not so effective yet further improvements in the catalytic efficiency are on the way.

3.5 Hydrolysis of furfuryl alcohol and integrated conversion of lignocellulosic biomass

After the optimization of the model hydrogenation, the hydrolysis of furfuryl alcohol was studied. This reaction could be easily achieved by refluxing furfuryl alcohol and hydrochloric acid in a mixed solvent of THF and water, and the yield of levulinic acid could reach 80%. The hydrolysis of furfuryl alcohol from lignocellulosic biomass was achieved by mixing the furfuryl alcohol solution (from section 3.4) with the liquid fraction after distillation (from section 3.2). We found that a supplement of catalyst acid (0.1 g, half of initial value) was needed to achieve the hydrolysis and the yield of levulinic acid achieved was 75%.

Finally, we studied the integrated conversion of five biomass feedstocks to levulinic acid. The process started from 1 g biomass raw material. The total mass yield of levulinic acid from bagasse was 26.1%, and this yield was much higher than the yield of levulinic acid from only C_6 carbohydrates (17.2 wt%). The extension of this process to other lignocellulosic biomass feedstocks was studied, and the results were listed in Table 5. The biggest improvement in the yield of levulinic acid was achieved for the conversion of corn cob (16.4 wt% to 28.3 wt%). However, the molar yields of levulinic acid from C_6 carbohydrates in poplar and pine were only 46.4% and 46.2%, and these results may be due to the difficulty associated with the depolymerization of the wood structure.

4. Conclusions

Overall, we have reported the integrated conversion of lignocellulosic biomass to levulinic acid in a biphasic system consisting of THF and NaCl aqueous solution. The one-step hydrolysis of C_6 and C_5 carbohydrates in the lignocellulosic biomass was firstly achieved to give a product solution that contained furfural, formic acid, levulinic acid and lignin, and the hydrolysis process was operated with both model substrates and biomass raw materials. The yields of the hydrolysis products are comparable to values obtained in the literature using a mixed solvent of GVL and water. In contrast to processes using the high boiling point solvent GVL, the utilization of THF allowed a one-step distillation of the product solution into three fractions: furfural and formic acid; levulinic acid; lignin. This separation step firstly removed the solid residue from the desired product effectively, and then let us investigate the hydrogenation of furfural with by-product formic acid without any interference. The hydrogenation process was eventually achieved and the product furfuryl alcohol was finally hydrolyzed to levulinic acid to achieve the integrated conversion of lignocellulosic biomass to levulinic acid. The highest mass yield of levulinic acid was 27.7%, which was promoted by 68.9% with the additional conversion of the hemicellulose fraction. Thus, the utilization of a lower boiling point solvent, THF, not only achieves the simultaneous hydrolysis of C_6 and C_5 carbohydrates in lignocellulosic biomass, but as compared to GVL, it also offers an alternative operation procedure for the integrated conversion of biomass to levulinic acid.

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