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One-pot conversion of biomass-derived xylose and furfural into levulinate esters *via* acid catalysis†

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Direct conversion of biomass-derived xylose and furfural into levulinic acid, a platform molecule, *via* acid-catalysis has been accomplished for the first time in dimethoxymethane/methanol. Dimethoxymethane acted as an electrophile to transform furfural into 5-hydroxymethylfurfural (HMF). Methanol suppressed both the polymerisation of the sugars/furans and the Aldol condensation of levulinic acid/ester.

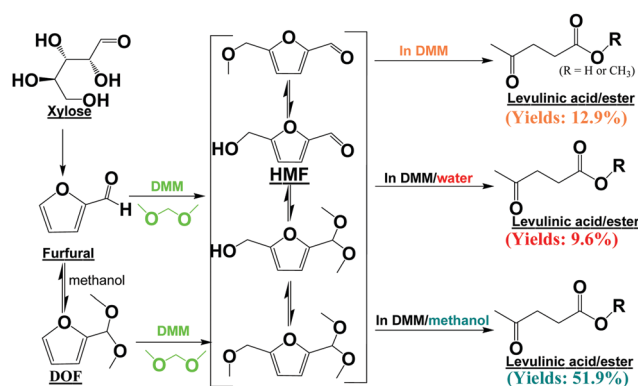
Levulinic acid is a building block chemical for the production of various value-added chemicals such as pharmaceuticals, plasticizers and various other additives.¹ Commercially, levulinic acid is produced from the hydrolysis of biomass in the presence of a mineral acid with yields ranging from 10 to 30 wt%.² The low yields of levulinic acid from biomass originate mainly from (1) the polymerisation of sugars during the conversion into levulinic acid³ and (2) the fact that only the C6 sugar substrates (glucose unit) in cellulose and hemicelluloses (mannose and galactose units) can be potentially converted into levulinic acid *via* acid catalysis.⁴ The C5 sugar substrates (xylose and arabinose units) under the same conditions are mainly converted into furfural,⁵ which is an intrinsic reason for the low yields of levulinic acid from biomass.

C5 sugars like xylose can be converted into levulinic acid,⁶ but *via* multiple steps, including the initial acid-catalyzed conversion to produce furfural in the liquid phase,⁷ the following partial hydrogenation of furfural to furfuryl alcohol in the gas⁸ or liquid phase⁹ and the subsequent acid-catalyzed conversion of furfuryl alcohol into levulinic acid/ester in the liquid phase.¹⁰ The above process involves both hydrogenation and acid-catalyzed reactions. It is preferable to avoid the hydrogenation step as it involves the use of hydrogenation catalysts, high pressure and hydrogen, making the process complicated and costly. A new strategy needs to be developed to achieve direct conversion of C5 sugars into levulinic acid under mild conditions.

The structural difference between HMF, the dehydration intermediate of C6 sugars,¹¹ and furfural, the dehydration intermediate of C5 sugars,¹² is the additional hydroxymethyl group in HMF. If one hydroxymethyl group could be added to the furan ring in furfural, furfural would then be able to be transformed into HMF, and subsequently into levulinic acid. The furan ring in furfural has aromaticity, and it is thus possible to introduce the hydroxymethyl group to furfural *via* electrophilic substitution.

In this study, we developed dimethoxymethane (DMM)/methanol as an effective reaction medium to transform xylose directly into levulinic acid/ester *via* only acid catalysis. The overall reaction pathways for the conversion of xylose into levulinic acid *via* acid catalysis are proposed in Scheme 1. The yields of levulinic acid/ester reached *ca.* 52% (150 °C, Amberlyst 70, in DMM/methanol), which was comparable to the yields of levulinic acid from glucose in water (*ca.* 50%, 180 °C, Amberlyst 70, in water).¹³ These are the new reaction routes for the direct conversion of xylose and furfural into levulinic acid under mild reaction conditions.

Entries 1–5 in Table 1 show the effects of reaction temperature on the formation of levulinic ester (LE) and levulinic acid (LA) from xylose in dimethoxymethane (DMM). The electrophilic substitution between DMM and furfural took place, transforming furfural



Scheme 1 Conversion of xylose to levulinic acid/ester in DMM/co-solvent. All the products were detected using GC-MS.

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Table 1 Conversion of xylose, glucose, furfural or HMF to levulinic acid (LA) and levulinic ester (LE)^a

Entry	Key parameters					Yields (%)		
	Reactants	Reaction medium	<i>T</i> (°C)	Catalyst(s)	<i>t</i> (min)	LE	LA	LE + LA
1	Xylose	DMM	140	A70	120	13.9	1.2	15.1
2	Xylose	DMM	150	A70	120	12.2	0.7	12.9
3	Xylose	DMM	160	A70	120	6.4	1.6	8.0
4	Xylose	DMM	170	A70	120	1.6	1.4	3.0
5	Xylose	DMM	180	A70	120	0.2	0.1	0.3
6	Xylose	DMM/water	150	A70	120	5.0	4.6	9.6
7	Xylose	DMM/DMSO	150	A70	120	0.2	0.4	0.6
8	Xylose	DMM/THF	150	A70	120	14.5	1.6	16.1
9	Xylose	DMM/diethyl ether	150	A70	120	13.6	0.9	14.5
10	Xylose	DMM/toluene	150	A70	120	19.7	1.7	21.4
11	Xylose	DMM/iso-propanol	150	A70	120	10.0	7.1	17.1
12	Xylose	DMM/methyl formate	150	A70	120	18.0	1.4	19.4
13	Xylose	DMM/ethanol	150	A70	120	22.6	2.1	24.7
14	Xylose	DMM/methanol (25/15) ^b	150	A70	120	22.8	2.1	24.9
15	Xylose	DMM/methanol (32.5/7.5)	150	A70	120	29.1	3.0	32.1
16	Xylose	DMM/methanol (29/11)	150	A70	120	32.6	2.2	34.8
17	Xylose	DMM/methanol (15/25)	150	A70	120	12.8	1.2	13.0
18	Xylose	DMM (40/0)	160	A70	120	6.4	1.6	8.0
19	Xylose	DMM/methanol (25/15)	160	A70	120	37.7	3.8	41.5
20	Xylose	DMM/methanol	150	A70	360	41.6	10.3	51.9
21	Xylose	DMM/methanol	160	La(III) ^c	120	3.1	0.3	3.4
22	Xylose	DMM/methanol	160	La(III) + A70	120	33.2	8.4	41.6
23	Xylose	Acetaldehyde	160	A70	120	0	0	0
24	Xylose	DEM/water	160	A70	120	4.4	2.6	7.0
25	Xylose	DEM/methanol	160	A70	120	27.4	4.0	31.4
26	Xylose	DEM/ethanol	160	A70	120	21.8	2.5	24.3
27	Glucose	DMM/methanol	160	A70	120	52.5	11.0	63.5
28	Glucose + xylose	DMM/methanol	160	A70	120	40.7	8.4	49.1
29	Furfural	DMM/methanol	160	A70	120	43.3	3.5	46.8
30	Furfural	DMM	160	A70	120	27.3	2.8	30.0
31	Furfural	DMM/water	160	A70	120	16.1	10.4	26.5
32	HMF	DMM/methanol	160	A70	120	61.7	11.9	73.6

^a Other reaction conditions: saccharide: 1.8 g; Amberlyst 70 (A70): 3.6 g; solvent: 40 mL; *t* = 120 min; *p* = autogenous vapour pressure. ^b The volume ratio of the solvents. The volumetric ratio for the mixed solvents with no parenthesis was 25 : 15. ^c La(III) stands for lanthanum(III) trifluoromethanesulfonate. The distribution of other products is summarized in Table S1 in the ESI.

into HMF or its derivatives (Fig. S1a in the ESI[†]). The concept of transforming furfural into HMF *via* electrophilic substitution in DMM was confirmed. However, the formation of LA or LE from xylose was not selective and the yields further decreased at higher reaction temperatures.

Furfural is highly reactive towards polymerization.¹⁴ Soluble polymers in the products were detected and their abundance increased with the reaction temperatures (Fig. S2, ESI[†]). Abundant ketone functionalities in the insoluble polymer were detected using FT-IR, especially above 150 °C (Fig. S3, ESI[†]). The polymerization of furfural was suspected to be the main reason for the low yields of levulinic acid/ester. DMM as the solvent/reactant alone was not able to prevent the polymerization. Co-solvents were thus employed herein to tackle the polymerizations of xylose/furfural in DMM.

Entries 6–14 in Table 1 show the effects of co-solvents on the yields of levulinic acid/ester. It was found that toluene also reacted with DMM to form aromatics (Scheme S1, ESI[†]), which was similar to the formation of HMF from furfural in terms of mechanism. This is because both the furan and benzene rings have aromaticity, and they could react with DMM *via* electrophilic substitution reactions. The reaction pathways for the transformation of furfural into the derivative of HMF are proposed in Scheme S2 (ESI[†]). Among the co-solvents investigated,

methanol or ethanol could remarkably promote the production of levulinic acid/ester (entries 13 and 14). The positive effects of alcohols on levulinic acid/ester formation were further investigated.

Entries 14–19 in Table 1 show the effects of methanol content in the reaction medium on levulinic acid/ester production. With the addition of a small amount of methanol to the reaction medium, the yields of levulinic acid/ester were more than doubled (entry 15 *versus* entry 2). Methanol could react with furfural, forming 2-(dimethoxymethyl)furan (DOF, the acetal of furfural) (Scheme 1). The formation of DOF destroyed the π -conjugation between the furan ring and the carbonyl group, which possibly made the furan ring more susceptible to the attack by the electrophile, facilitating the subsequent electrophilic substitution reaction. More importantly, methanol significantly suppressed the polymerization reactions. As evidenced in Fig. 1a, the abundance of the soluble polymers decreased remarkably with methanol as the co-solvent.

Entries 20–28 in Table 1 show the conversion of xylose/glucose *versus* reaction time, catalysts and electrophiles. The formation of levulinic acid/ester was favored by a longer residence time (entry 20). The Lewis acid catalyst was not active for the conversion of xylose to levulinic acid/ester (entry 21), but was active for the polymerization reactions (Fig. S4, ESI[†]). A combination of the Lewis acid with A70 (Brønsted acid) did not improve the



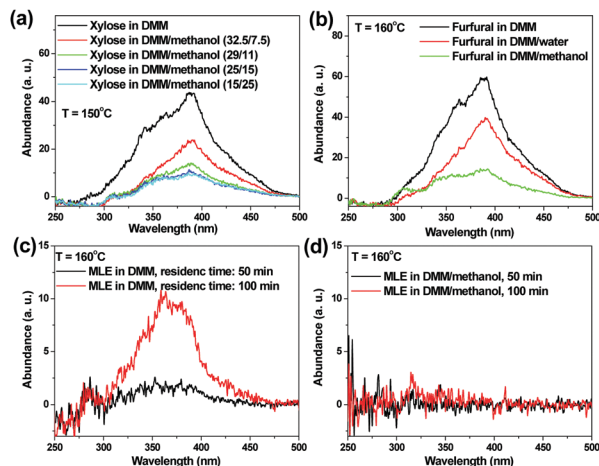


Fig. 1 Constant energy (-2800 cm^{-1}) synchronous spectra of the soluble polymers formed from the acid-catalyzed conversion of xylose, furfural and methyl levulinate (MLE) in DMM or DMM/methanol.

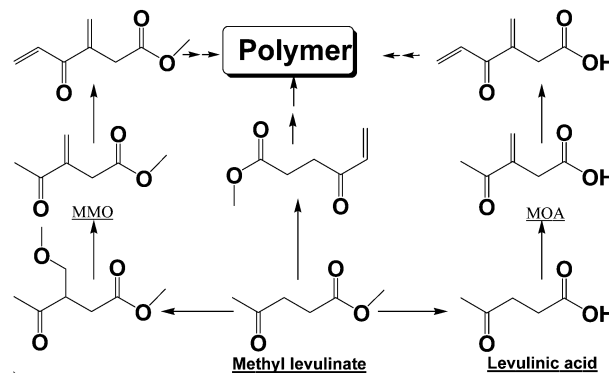
performance (entry 22 *versus* entry 19). Acetaldehyde as the electrophile could not trigger the transformation of furfural into HMF. In diethoxymethane (DEM)/water, the levulinate ester produced was switched to ethyl levulinate (entry 9), indicating that the ethoxy group from DEM was transferred into the product. Methanol or ethanol as the co-solvent of DEM promoted the formation of the levulinic esters.

When glucose was used as a reactant, levulinic acid/ester yields reached *ca.* 63.5% (entry 27), which was higher than that in water (*ca.* 50%).¹³ For mixed glucose/xylose, half of them were converted to levulinic acid/ester (entry 28). In this process, neither hydrogen nor a hydrogenation catalyst was required. Using only an acid catalyst and DMM/methanol, the simultaneous conversion of both the C5 and C6 sugars into levulinic acid/ester was achieved. The conversion of the biomass-derived furans into levulinic acid/ester was also investigated in DMM/methanol.

Entries 29–32 in Table 1 show the formation of levulinic acid/ester from furfural and HMF. With DMM/methanol as the reaction medium, the polymerization reactions could be effectively suppressed (Fig. 1b). However, the yields of levulinic acid/ester from furfural could not reach 50% (entry 29), which was similar to that from xylose (entry 19).

Clearly, whether xylose or furfural was used as the starting reactant made no marked difference in terms of the yields of levulinic acid/ester (entries 19 and 29), which was also confirmed by the conversion of xylose or furfural *versus* the reaction time (Fig. S5–S7, ESI[†]). Thus, the polymerization during the conversion of xylose to furfural was not the main reason for the loss of levulinic acid/ester production. Other undesirable reactions must be responsible. The soluble polymers formed from furfural or HMF in DMM/methanol were very different from those in water (Fig. S8, ESI[†]), indicating the involvement of polymerization other than that from xylose or furfural.

Levulinic acid and methyl levulinate have a ketonic group and active α -H, making them very active in polymerization reactions. It was found that the formation of levulinic acid/ester from xylose (Fig. S5, ESI[†]) or furfural (Fig. S6, ESI[†]) was always accompanied



Scheme 2 Condensation of methyl levulinate in DMM. All the compounds except the polymer were detected using GC-MS.

by the formation of methyl 3-methylene-4-oxopentanoate (MMO) (Fig. S1, ESI[†]) and polymers (Fig. S7 and S8, ESI[†]), especially at elevated reaction temperatures where the yields of levulinic acid/ester were low. MMO was identified by interpretation of its mass spectrum (Schemes S3 and S4, ESI[†]), which was produced *via* the Aldol condensation between methyl levulinate and DMM. Other compounds formed *via* similar routes were also identified (Scheme 2).

The formation of MMO and other condensation products consumed the methyl levulinate produced and led to the polymer formation (Fig. S7, ESI[†]), which diminished the production of levulinic acid/ester from xylose or furfural. The abundance of MMO in DMM was thrice as high as that in DMM/methanol. Evidently, the presence of methanol suppressed the Aldol condensation of levulinic acid/ester and preserved them in the reaction medium. This was further verified by the experiments with methyl levulinate as the starting reactant.

With methanol as the co-solvent, although MMO was still formed (Table S2, ESI[†]), the conversion of methyl levulinate was much smaller (Fig. 2). Evidently, the polymerization of methyl levulinate was suppressed in the presence of methanol. Aldol condensation was the main route for the polymerization of methyl levulinate in DMM, leading to the formation of the polymers with conjugated π -structures and extended size (Fig. 1c). Herein we demonstrated that methanol could suppress the Aldol condensation reaction, suppressing the polymer formation (Fig. 1d) and preserving levulinic acid/ester in the reaction medium.

Other reaction parameters in the conversion of xylose/furfural in DMM/methanol were also investigated. The mass transfer limitation was insignificant at stirring rates above 300 rpm (Fig. S9, ESI[†]). A70 has a limited capacity to catalyse the conversion of xylose with high loading (Fig. S10, ESI[†]), due to deactivation induced by the polymer formation (Fig. S11 and S12, ESI[†]). The recycle tests with xylose (Fig. S13, ESI[†]) or furfural (Fig. S14, ESI[†]) as the starting reactant confirmed the deactivation of A70. Both soluble (Fig. S15 and S16, ESI[†]) and insoluble polymers (Fig. S17, ESI[†]) were formed, which significantly reduced the acid density of A70 (Fig. S18, ESI[†]). The functionalities of the soluble polymer include aromatic ring structures, α - β unsaturated carbonyls and carbon double bonds (Fig. S19, ESI[†]). The insoluble polymer



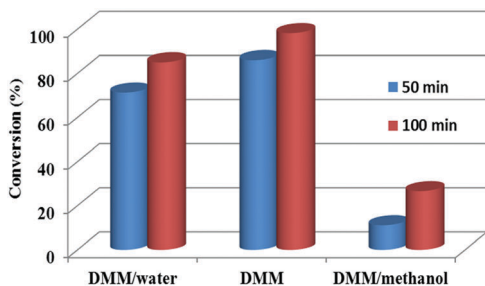


Fig. 2 Conversion of methyl levulinate in DMM/water, DMM and DMM/methanol at reaction times of 50 and 100 min. Reaction conditions: methyl levulinate: 1.8 g; A70: 3.6 g; DMM/co-solvent: 40 mL (volume ratio; 25 : 15); $T = 160\text{ }^{\circ}\text{C}$.

has similar functionalities (Fig. S17, ESI[†]) and thermal stability to A70 (Fig. S20, ESI[†]).

To summarize, a new route for the one-pot conversion of biomass-derived C5 sugars and furans into levulinic acid/ester has been demonstrated. The method is very simple. No hydrogen or hydrogenation catalyst is needed. Only an acid catalyst with DMM/methanol as the reactant/solvent is required to achieve the direct conversion of the C5 sugars to levulinic acid/ester. In this method, DMM is the electrophile to transform furfural into HMF *via* electrophilic substitution reactions. Methanol as the co-solvent/reactant played multiple critical roles: (1) it promoted the electrophilic substitution of furfural to produce HMF or the derivatives of HMF; (2) it suppressed the polymerization reactions of the sugars in the acidic reaction medium; and (3) it suppressed the Aldol condensation of levulinic acid/ester with DMM. Using the developed method, the cellulose-derived C6 sugars, the hemicelluloses-derived C5 sugars and the furans (furfural, HMF) all can be converted to the same products, levulinic acid/ester, *via* the same acid catalysis process. This drastically enhances the efficiency for the production of levulinic acid/ester from biomass, the platform molecules for chemical diversity and biofuel production.

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