

Catalytic conversion of raw *Dioscorea composita* biomass to 5-hydroxymethylfurfural using a combination of metal chlorides in *N*,*N*-dimethylacetamide solvent containing lithium chloride

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Abstract We synthesized 5-hydroxymethylfurfural (HMF) from carbohydrates using metal chloride catalysts. A 33.2 % yield of HMF was obtained from raw *Dioscorea composita* biomass with high starch by using a catalyst system composed of CrCl₃·6H₂O and LaCl₃·6H₂O at 120 °C for 4 h in *N*,*N*-dimethylacetamide containing lithium chloride. The catalyst system is also cost-effective for the conversion of soluble starch into HMF. In addition, levulinic acid was not formed in the reactions.

Keywords Dioscorea composita · Soluble starch · Glucose · Metal chlorides · 5-Hydroxymethylfurfural

Introduction

Diminishing fossil fuel reserves, severe environmental pollution, and a deteriorating ecosystem have aroused the attention of people to renewable energy resources [1, 2]. In chemical industries, abundant biomass resources such as carbohydrates are being studied as potential renewable carbon sources for liquid fuels and other valuable chemicals [3–6]. In particular, 5-hydroxymethylfurfural (HMF), a six-carbon furan ring produced from carbohydrate dehydration, has gradually become a key chemical platform [6–10]. Recent efforts have focused on converting carbohydrates to HMF. Fructose is a preferred feedstock for high HMF yield.

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Building of a biorefinery platform based on HMF requires huge amounts of inexpensive, renewable, and raw non-food materials containing glucose [6], such as non-food plants rich in starch. Starch is a polysaccharide that is widely available in nature and at relatively lower cost than other sugars such as fructose and glucose; And besides, hydrolysis of starch is favored over that of cellulose [11]. *Dioscorea composita* is rich in starch (ca. 64–75 % by dry weight) and no systematic farming is required. It could be a good sustainable biomaterial for the industrial production of HMF. We aimed to exploit a catalytic system for direct transformation of raw *D. composita* biomass into HMF.

Few studies have been conducted on the possibility of starch for potential HMF production. Mineral acids [12], solid acids [13], and metallic compounds [14–19] have been utilized as catalysts for starch dehydration in multiple reaction media, including biphasic water-organic systems and ionic liquids. Chheda et al. [12] claimed that 26 % HMF yield from starch can be achieved using HCl as a catalyst under a biphasic system. Yang et al. [14] also studied starch transformation into HMF using AlCl₃·6H₂O under a biphasic system composed of an aqueous phase saturated with NaCl and an organic extracting-phase tetrahydrofuran, and an HMF yield of 50 % was achieved; however, the HMF yields are relatively low, primarily because these catalysts are unsuitable for isomerization of glucose to fructose in an aqueous phase. Ionic liquid catalytic systems have also been developed for starch conversion to HMF in high yield, except for biphasic systems. Hu et al. [16] found that HCl and CrCl₂ in 1-octyl-3-methylimidazolium chloride was an effective catalytic system that can efficiently convert starch to HMF with a yield of 73.0 %. Considering that ionic liquids are expensive, a catalytic system that can convert starch to HMF in high yield at low energy cost may be developed.

Chromium catalysts in alkylimidazolium chloride ionic liquids or an N,Ndimethylacetamide (DMA) system enable catalyzed production of HMF from glucose, sucrose, and cellulose in good yields [20–23]. Lanthanide (III) ions can also efficiently catalyze dehydration of fructose into HMF in organic solvents, such as dimethyl sulfoxide (DMSO) [24]. A work by Yi et al. [17] on the efficient conversion of raw tapioca root biomass with high starch to HMF using chromium (III) chloride as the catalyst provided further information on HMF formation. In the present paper, we report a cost-effective catalytic system for HMF synthesis from D. *composita* biomass based on dehydration of glucose and maltose into HMF. The catalytic system is composed of a combination of chromium (III) chloride and lanthanide (III) chloride in DMA-LiCl. This system facilitates access to fuels and chemicals derived from HMF.

Experimental

General

Commercial chemicals were of analytical grade or better and were used without further purification. All reactions were performed in glass flasks heated in a temperature-controlled oil bath with magnetic stirring.

D. composita was purchased from Xishuangbanna Samost Technology Co., Ltd. (Xishuangbanna, China). Soluble starch, maltose·H₂O, glucose, CrCl₃·6H₂O, LaCl₃·6H₂O, AlCl₃, LiCl, DMA, *N*,*N*-dimethylformamide (DMF), DMSO, and levulinic acid were of analytical grade and obtained from Tianjin Chemical Reagent Company (Tianjin, China). A standard sample of HMF (99 %) was obtained from Sigma-Aldrich Company (USA). *D. composita*, soluble starch, maltose, and glucose were dried to constant weight at 60 °C prior to use.

HMF synthesis from sugars

In a typical run, glucose (1 g, 5.6 mM), $CrCl_3 \cdot 6H_2O$ (5 mol% to glucose) and $LaCl_3 \cdot 6H_2O$ (2.5 mol% to glucose) were added into DMA (10 mL). The mixture was heated at 100 °C for 0.5–2.5 h with a magnetic stirrer. Reactions with maltose were similar except that maltose (1 g, 5.6 mM glucose units), $CrCl_3 \cdot 6H_2O$ (10 mol% with respect to glucose contained in the maltose) and $LaCl_3 \cdot 6H_2O$ (5 mol% with respect to glucose contained in the maltose) were mixed in DMA.

HMF synthesis from soluble starch and D. composita

Soluble starch (1 g, 5.84 mmol glucose units) was suspended in 25 mL of DMA and kept at 160 °C for 1 h under continuous stirring. After the slurry had been allowed to cool to 100 °C, 2 g of anhydrous LiCl was added [25–27]. The mixture was heated at 80 °C for 0.5 h under continuous stirring to form a viscous solution. Then, $CrCl_3 \cdot 6H_2O$ (30 mol% with respect to glucose contained in the soluble starch) and $LaCl_3 \cdot 6H_2O$ (15 mol% with respect to glucose contained in the soluble starch) were mixed in the solution. The reaction mixture was stirred at 100–140 °C for 1–5 h. Reactions with *D. composita* were similar except that *D. composita* (1 g, 64.64 % starch, 4 mmol glucose units) was dissolved into 50 mL of DMA containing 4 g of anhydrous LiCl. For soluble starch and *D. composita*, HMF yields are defined as follows: HMF yield = moles of HMF produced/moles of starting glucose units.

Product analysis

The analysis of product HMF was conducted with an HP6890/5973 N gas chromatograph-mass spectrometer (GC-MS) equipped with an HP-5MS capillary column (30 m × 0.25 mm × 0.25 µm), with the following analysis conditions: detector temperature, 280 °C; injection temperature, 280 °C; carrier gas, argon; flow rate of carrier gas, 1.0 mL/min. The chemical structure of product HMF was characterized by Fourier transform infrared spectroscopy (FT-IR, Nicolet Nexus 670, Nicolet, USA) at an optical range of 400–4000 cm⁻¹ and a resolution of 8 cm⁻¹ (Fig. S5 in Supporting Information). The product HMF was further characterized by nuclear magnetic resonance (NMR) analysis (Avance III 400, Bruker, USA; Figs. S3, S4 in Supporting Information). The sugars from the dehydration of soluble starch were also characterized by FT-IR and the sugar samples were precipitated by an ethanol extraction method. Levulinic acid was estimated by using vanillic aldehyde as the indicator of the spectral measure study.

Vanillic aldehyde can react with levulinic acid, thereby resulting in a change in colour from colorless to blue-green.

Results and discussion

HMF synthesis from glucose

The reactivity of glucose in DMA was first explored with a single metal chloride catalyst ($CrCl_3 \cdot 6H_2O$, $AlCl_3$), and reactions were performed at 80–100 °C for 0.75 h. The results are shown in Table 1. Glucose was converted to HMF in

Entry	Solvent	Catalyst (mol%)	Co-catalyst (mol%)	T (°C)	Time (h)	Molar yield (%)
1	DMSO	CrCl ₃ ·6H ₂ O, 5		100	0.75	1.5
2	DMF	CrCl ₃ ·6H ₂ O, 5		100	0.75	1.5
3	DMA	CrCl ₃ ·6H ₂ O, 5		100	0.75	30.4
4	DMA	CrCl ₃ ·6H ₂ O, 5		80	0.75	6.1
5	DMA	CrCl ₃ ·6H ₂ O, 5		100	1.5	56.9
6	DMA	AlCl ₃ ·6H ₂ O, 5		80	0.75	1.5
7	DMA	AlCl ₃ ·6H ₂ O, 5		100	0.75	7.3
8	DMA	AlCl ₃ ·6H ₂ O, 5		100	1.5	16
9	DMA	CrCl ₃ ·6H ₂ O, 5	LaCl ₃ ·6H ₂ O, 2.5	80	0.75	1.5
10	DMA	CrCl ₃ ·6H ₂ O, 5	LaCl ₃ ·6H ₂ O, 2.5	100	0.75	40.7
11	DMA	CrCl ₃ ·6H ₂ O, 5	LaCl ₃ ·6H ₂ O, 2.5	100	1.5	77.6
12	DMA	LaCl ₃ ·6H ₂ O, 2.5		100	0.75	1.5
13	DMA	LaCl ₃ ·6H ₂ O, 2.5		100	1.5	6.3
14	DMA	CrCl ₃ ·6H ₂ O, 5	AlCl ₃ ·6H ₂ O, 2.5	80	0.75	8.2
15	DMA	CrCl ₃ ·6H ₂ O, 5	AlCl ₃ ·6H ₂ O, 2.5	100	0.75	17.4
16	DMA	CrCl ₃ ·6H ₂ O, 5	AlCl ₃ ·6H ₂ O, 2.5	100	1.5	73.1
17	DMA	CrCl ₃ ·6H ₂ O, 6.82	LaCl ₃ ·6H ₂ O, 0.68	100	0.75	28.7
18	DMA	CrCl ₃ ·6H ₂ O, 6.25	LaCl ₃ ·6H ₂ O, 1.25	100	0.75	27.8
19	DMA	CrCl ₃ ·6H ₂ O, 5.62	LaCl ₃ ·6H ₂ O, 1.88	100	0.75	31.9
20	DMA	CrCl ₃ ·6H ₂ O, 3.75	LaCl ₃ ·6H ₂ O, 3.75	100	0.75	25
21	DMA	CrCl ₃ ·6H ₂ O, 2.5	LaCl ₃ ·6H ₂ O, 5	100	0.75	24.4
22	DMA	CrCl ₃ ·6H ₂ O, 1.5	LaCl ₃ ·6H ₂ O, 6	100	0.75	18.5
23	DMA	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	100	0.75	41.5
24	DMA	CrCl ₃ ·6H ₂ O, 5	LaCl ₃ ·6H ₂ O, 2.5	100	0.5	15.3
25	DMA	CrCl ₃ ·6H ₂ O, 5	LaCl ₃ ·6H ₂ O, 2.5	100	1	40.8
26	DMA	CrCl ₃ ·6H ₂ O, 5	LaCl ₃ ·6H ₂ O, 2.5	100	1.5	77.6
27	DMA	CrCl ₃ ·6H ₂ O, 5	LaCl ₃ ·6H ₂ O, 2.5	100	2	44.1
28	DMA	$CrCl_3 \cdot 6H_2O, 5$	LaCl ₃ ·6H ₂ O, 2.5	100	2.5	40

Table 1 HMF synthesis from glucose

Glucose (1 g, 5.6 mM), solvent (10 mL). Catalyst loading and co-catalyst loading is relative to glucose. Yields are based on GC–MS analysis

moderate yields (0–30.4 %; entries 3–4, 6–7). The results were negative to some extent even though the yields were higher at 100 °C than at 80 °C. As a next attempt, reactions for longer reaction time (1.5 h) were investigated with increased HMF yields (entries 5, 8). In particular, $CrCl_3·6H_2O$ yielded 56.9 % HMF at 100 °C for 1.5 h (entry 5). By contrast, a lesser amount of HMF was obtained with AlCl₃ catalyst (entry 8). Nonetheless, the catalyst system, composed of $CrCl_3·6H_2O$ and DMA, was effective for HMF synthesis compared with yields of up to 70 % achieved in 1-alkyl-3-methylimidazolium chloride [20]. In another attempt, glucose transformation into HMF was catalyzed by $CrCl_3·6H_2O$ in DMF or DMSO at 100 °C for 0.75 h. The HMF yields were nearly 1.5 % in both cases (entries 1–2).

Based on the above results, glucose conversion into HMF under single metal chloride conditions was not perfect. Given the recent results on the efficient catalytic activity of lanthanide (III) ions for saccharide conversion to HMF [24], LaCl₃·6H₂O was used with CrCl₃·6H₂O (molar ratio between two metal chlorides is $CrCl_3 \cdot 6H_2O:LaCl_3 \cdot 6H_2O = 2:1$) to enhance the ability of glucose transformation into HMF. The reactions were operated at 80-100 °C for 0.75-1.5 h (entries 9-11). The HMF yields were expectedly increased, and all the HMF yields were higher than those in the presence of a single metal chloride. Moreover, levulinic acid was not formed (no change in color from colorless to blue-green) when LaCl₃·6H₂O was added as a co-catalyst. Intrigued by the LaCl₃·6H₂O effect, we investigated glucose dehydration catalyzed by single LaCl₃·6H₂O (entries 12–13). All the HMF yields were unexpectedly not more than 6.3 %. The known catalytic activity of lanthanide (III) ions for glucose conversion to HMF [18, 24] along with our observations of glucose reactivity catalyzed by single LaCl₃·6H₂O indicated that CrCl₃·6H₂O leads to glucopyranose isomerization into fructofuranose. This process is followed by dehydration catalyzed by a combination of CrCl₃·6H₂O and LaCl₃·6H₂O (Fig. 1). However, the reason why the catalytic performance was enhanced when addition of LaCl₃ as co-catalysts still needs further investigation. In another attempt, glucose conversion was investigated in the presence of CrCl₃·6H₂O and AlCl₃ at 80-100 °C for 0.75–1.5 h (entries 14–16). AlCl₃ is less effective for glucose conversion to HMF than LaCl₃·6H₂O. (AlCl₃ only effectively catalyzes the isomerization of glucose to fructose in aqueous solution [14]).

The effect of molar ratio between $CrCl_3 \cdot 6H_2O$ and $LaCl_3 \cdot 6H_2O$ (10 mol% to glucose, total equivalent of two metal chlorides) was studied next. A series of molar ratios from 10:1 ($CrCl_3 \cdot 6H_2O$:La $Cl_3 \cdot 6H_2O$) to 1:4 were screened. The reactions were conducted at 100 °C for 0.75 h (entries 17–22). Based on the results, either the amount of La $Cl_3 \cdot 6H_2O$ was gradually increased from a molar ratio of 2:1 to 1:4 or reduced from 2:1 to 1:10, and all HMF yields were lower than 40.7 %. The optimal molar ratio of $CrCl_3 \cdot 6H_2O$ and $LaCl_3 \cdot 6H_2O$ can more effectively lead to glucopyranose isomerization to fructofuranose than $LaCl_3 \cdot 6H_2O$ and $LaCl_3 \cdot 6H_2O$. A 41.5 % HMF yield was then obtained when the amount of catalyst was doubled (entry 23). In addition, time-course experiments of HMF synthesis using $CrCl_3 \cdot 6H_2O$ and $LaCl_3 \cdot 6H_2O$ were performed. The maximum HMF yield can be



Fig. 1 Hydrolysis of carbohydrates into glucose using a combination of metal chlorides in DMA. Chromium species, depicted here as a hexacoordinate chromium (III) complex, catalyze the isomerization of glucose into fructose through a putative enediolate intermediate, followed by dehydration to HMF using a combination of metal chlorides in solvent. And levulinic acid wasn't formed in the reactions

achieved at 77.6 % after 1.5 h (entry 26), and prolonged reaction led to decreased HMF yields because of HMF conversion to byproducts such as humins [22].

HMF synthesis from maltose

In our study, HMF synthesis without any catalysts was first attempted at 120 °C for 2 h, and the HMF yield was only 4.8 % (entry 10; Table 2). Subsequently, the HMF synthesis catalyzed by the combination of $CrCl_3 \cdot 6H_2O$ and $LaCl_3 \cdot 6H_2O$ (7.5 mol% to glucose unit in maltose; entry 1) was performed, and only 31.7 % HMF yield was obtained at 100 °C for 1.5 h. Given that disaccharide conversion to HMF involves the following steps: (1) hydrolysis breaks the glycosidic bond, converting disaccharides into glucose and fructose; (2) glucose is isomerized into fructose; and (3) fructose is dehydrated to form HMF (Fig. 1) [6]. The lower yield for maltose is attributed to the to difficultly of breaking the glycosidic bond as compared with the glucose (entry 26; Table 1). Therefore, we sought to utilize the catalytic system

Entry	Solvent	Catalyst (mol%)	Co-catalyst (mol%)	T (°C)	Time (h)	Molar yield (%)
1	DMA	CrCl ₃ ·6H ₂ O, 5	LaCl ₃ ·6H ₂ O, 2.5	100	1.5	31.7
2	DMA	CrCl ₃ ·6H ₂ O, 7.5	LaCl ₃ ·6H ₂ O, 3.75	100	1.5	38.1
3	DMA	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	100	1.5	45.2
4	DMA	CrCl ₃ ·6H ₂ O, 12.5	LaCl ₃ ·6H ₂ O, 6.25	100	1.5	44.7
5	DMA	CrCl ₃ ·6H ₂ O, 15	LaCl ₃ ·6H ₂ O, 7.5	100	1.5	43.4
6	DMA	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	100	0.5	3.1
7	DMA	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	100	1	8.3
8	DMA	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	100	2	27.1
9	DMA	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	100	2.5	26.1
10	DMA			120	2	4.8
11	DMA	HCl, 5		100	1.5	3.8
12	DMA	HC1, 20		100	1.5	23.3
13	DMA	HCl, 5		120	1.5	14.5
14	DMA	HC1, 20		120	1.5	32.8

Table 2 HMF synthesis from maltose

Maltose (1 g, 5.6 mM glucose units), DMA (10 mL). Catalyst loading and co-catalyst loading is relative to glucose units contained in the maltose. Yields are based on GC–MS analysis

of CrCl₃·6H₂O and LaCl₃·6H₂O to convert maltose into HMF in DMA. Next, the effect of catalyst and co-catalyst loading on maltose dehydration was investigated (molar ratio of CrCl₃·6H₂O and LaCl₃·6H₂O was 2:1; entries 2–5). The HMF yields were increased from 31.7 to 45.2 % when the catalyst and co-catalyst loadings varied from 7.5 to 15 mol%. Moreover, the HMF yields did not significantly differ when the catalyst and co-catalyst loadings were higher than 15 %. The effect of reaction time on maltose dehydration was also tested to better understand the catalytic system (entries 6–9). The HMF yields became higher along with increasing time from 0.5 to 1.5 h. However, when the reaction time was extended to 1.5 h or longer, the HMF yield decreased to some extent because of HMF conversion byproducts such as humins [22]. Furthermore, the HMF synthesis from maltose using hydrochloric acid as the catalyst was reported, and a 32.8 % HMF yield was achieved in the presence of 20 mol% hydrochloric acid at 120 °C for 1.5 h (entry 14). By contrast, the best performance of HMF yield at 45.2 % was realized under milder and less acidic (corrosive) condition (entry 3).

HMF synthesis from soluble starch and D. composita

Starch is a polyglucan linked with glucose units through α -glycosidic linkages. In addition to the challenge of glucose isomerization to fructose, two most important factors must be considered for industrial applications; that is, the reduced solubility in almost all solvents and glycosidic bonds are difficult to break. However, we suspected that the solubility of soluble starch in DMA-LiCl and the efficient conversion of glucose and maltose into HMF with the combination of CrCl₃·6H₂O

Entry	Solvent	Catalyst (mol%)	Co-catalyst (mol%)	T (°C)	Time (h)	Molar yield (%)
1	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	100	1.5	2.3
2	DMA-LiCl(8.5 %wt)	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	120	1.5	4.3
3	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	120	3	19
4	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 10	LaCl ₃ ·6H ₂ O, 5	140	1.5	18.6
5	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 20	LaCl ₃ ·6H ₂ O, 10	120	1.5	6.5
6	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	1.5	8.7
7	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 40	LaCl ₃ ·6H ₂ O, 20	120	1.5	8.8
8	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	1	3.5
9	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	2	12.4
10	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	3	52.2
11	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	4	54.5
12	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	5	53.4
13	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	1	8.6
14	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	2	12.9
15	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	3	31.7
16	DMA-LiCl (8.5 %wt)	CrCl ₃ ·6H ₂ O, 30	LaCl ₃ ·6H ₂ O, 15	120	4	33.2
17	DMA-LiCl (8.5 %wt)	$CrCl_3 \cdot 6H_2O$, 30	LaCl ₃ ·6H ₂ O, 15	120	5	33.3

Table 3 HMF synthesis from soluble starch and D. composita

Soluble starch (1 g, 5.84 mM glucose units, entries 1–12), *D. composita* (1 g, 64.64 % starch, 4 mM glucose units, entries 13–17) The weight percent of LiCl is relative to DMA (entries 1–12; DMA, 25 mL; entries 13–17, DMA, 50 mL). Catalyst loading and co-catalyst loading is relative to glucose units contained in the polysaccharides. Yields are based on GC–MS analysis



Fig. 2 The FT-IR spectra of soluble starch and D. composita

and LaCl₃· $6H_2O$ can achieve superior results. The HMF yield from soluble starch was up to 54.5 % within 5 h at 120 °C (entries 8–12; Table 3). These yields agreed well with the reports of HMF synthesis from starch by Yang et al. [14] and Hu et al.



Fig. 3 The FT-IR spectra of analytical grade sugars and the hydrolysis product of starch. A sample from the reaction mixture containing sugars (Table S1, entry 2) is precipitated by an ethanol extraction method

[15]. We then discovered another desirable attribute of the present process: the ready conversion of *D. composita* with high starch content. For the conversion of untreated *D. composita*, 33.2 % HMF yield was significantly obtained at 120 °C for 4 h (entry 16). Levulinic acid was not formed in all experiments. The physicochemical changes of the extractant derived from soluble starch were characterized using FT-IR to explore the scheme of HMF formation from starch in DMA-LiCl. Figure 2 shows the FT-IR spectral profiles of the *D. composita* and analytical grade soluble starch. The absorption bands of the raw biomass by the C–O–C and C–OH stretching modes that are typically observed in carbohydrates such as starch were identified in the 900–1200 cm⁻¹ regions [28, 29]. The banding pattern of the raw biomass was very similar with that of soluble starch, indicating that the main biomass composition is starch. Based on the determination of total

reducing sugar through the dinitrosalicylic acid (DNS) method (Table S1 in Supporting Information), the sugars in the reaction mixture (Table S1, entry 2) were characterized using an FT-IR spectrometer. As shown in Fig. 3, the new absorption peak at 1020 cm⁻¹ for the sample is attributed to the bending vibration of the hydroxyl group in mono- and disaccharides [30]. This shift in the absorbance signals is probably caused by starch depolymerization into smaller molecules such as glucose or maltose (the absorbance band around the 1020 cm⁻¹ region is frequently found from glucose and maltose standards; Fig. 3). Given the results on sugar conversion and reports in the literature, we propose that the supposed scheme of HMF formation from starch in DMA-LiCl is the following (Fig. 1): (1) starch hydrolysis into maltose and glucose catalyzed by the combination of CrCl₃·6H₂O; and (3) fructose dehydration to form HMF catalyzed by the combination of CrCl₃·6H₂O and LaCl₃·6H₂O. However, further investigation is needed to confirm this mechanism.

Conclusion

Effective catalytic conditions for *D. composita* transformation into HMF were achieved using $CrCl_3 \cdot 6H_2O$ and $LaCl_3 \cdot 6H_2O$ in DMA-LiCl. The cost-effective catalytic system has an excellent potential for industrial application. Further mechanistic studies of the reactions involved are beneficial for the exploitation of non-food plants containing starch as raw materials for renewable energy and chemical industries.

Compliance with ethical standards

Conflict of interest The authors have declared no conflict of interest.

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