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One-Pot Conversions of Lignocellulosic and Algal Biomass into Liquid Fuels

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The one-pot conversion of lignocellulosic and algal biomass into a liquid fuel, 2,5-dimethylfuran (DMF), has been achieved by using a multicomponent catalytic system comprising $[DMA]^+[CH_3SO_3]^-$ (DMA = *N*,*N*-dimethylacetamide), Ru/C, and formic acid. The synthesis of DMF from all substrates was carried out under mild reaction conditions. The reaction progressed via 5-hydroxyemthylfurfural (HMF) in the first step followed by hydrogenation and hydrogenolysis of HMF with the Ru/C catalyst and formic acid as a hydrogen source. This report discloses the effectiveness of the Ru/C catalyst for the first time for DMF synthesis from inexpensive and readily abundant biomass sources, which gives a maximum yield of 32% DMF in 1 h. A reaction route involving 5-(formyloxymethyl)furfural (FMF) as an intermediate has been elucidated based on the ¹H and ¹³C NMR spectroscopic data. Another promising biofuel, 5-ethoxymethylfurfural (EMF), was also synthesized with high selectivity from polymeric carbohydrate-rich biomass substrates by using a Brønsted acidic ionic liquid catalyst, that is [DMA]⁺[CH₃SO₃]⁻, by etherification of HMF in ethanol.

Introduction

The conversion of abundant and renewable lignocellulose into liquid fuels for transport applications is the aspiration of current bioenergy research.^[1,2] A long-standing issue is to produce liquid fuels from renewable sources including cellulose and lignocellulosic biomass by an economically and environmentally acceptable route.^[3,4] The chemical transformation of biomass into biofuel involves a multistep process, namely, 1) pretreatment of biomass into cellulosic components, 2) acid-catalyzed hydrolysis of cellulose into sugar components and 3) catalytic transformation of sugars into fuel components via 5-hydroxymethylfurfural (HMF) as an intermediate.^[5] Recent studies have shown that lignocellulosic biomass can be dissolved in an ionic liquid (IL) and converted into fuels without the need to isolate the cellulosic components.^[6] Dumesic et al. first reported the synthesis of 2,5-dimethylfuran (DMF), a promising liquid fuel, from fructose by hydrogenation-hydrogenolysis of the HMF intermediate.^[7]

Bioethanol, the only renewable liquid fuel currently produced in large quantities, suffers from several limitations, including low energy density, high volatility, and contamination by the absorption of atmospheric water. Compared to bioethanol, DMF is considered as an ideal liquid fuel because of its superior energy density (30 kJ cm⁻³) and high research octane number (RON = 119).^[8] DMF is immiscible with water and easier to blend with gasoline than ethanol. Recently, biomassderived DMF has been successfully tested as a biofuel in a single-cylinder gasoline direct-injection (GDI) research engine.^[9] The performance of DMF was satisfactory against gasoline in terms of combustion, ignition, and emission characteristics. 5-Ethoxymethyl-2-furfural (EMF)^[10] is another promising biofuel with a high boiling point (235 °C) and comparable energy density (8.7 kWhL⁻¹) to that of standard gasoline (8.8 kWh L⁻¹) and diesel (9.7 kWh L⁻¹).^[11] EMF was prepared via 5-chloromethylfurfural from sugar and biomass.^[12,13] However, these processes involved multistep reactions and required an additional separation step. Recently, EMF was synthesized from macroalgae-derived agar^[14] and sugar derivatives using acidic IL catalysts.^[15]

As reported by Dumesic et al., the first step of the direct conversion of fructose to DMF (71% yield) involved acid-catalyzed dehydration to HMF followed by hydrogenation and hydrogenolysis of HMF with a Cu-Ru/C catalyst.^[7] Binder and Raines reported the synthesis of DMF from untreated corn stover, giving a 9% DMF vield based on the cellulose content of the corn stover.^[16] This two-step synthesis of DMF involved the CrCl₃-HCl-catalyzed transformation of corn stover into HMF, followed by hydrogenation-hydrogenolysis of HMF to DMF by the Cu-Ru/C catalyst in the presence of H₂. In this process, a toxic chromium salt along with a mineral acid was used as the catalyst for the degradation of corn stover into HMF. Recently, Yang and Sen reported the conversion of biomass-derived carbohydrates to 5-methylfurfural (MF)^[17] and a promising liquid fuel 2,5-dimethyltetrahydrofuran (DMTHF)^[18,19] with good yields using homogeneous RuCl₃ and RhCl₃ catalysts. The same authors have also used a heterogeneous Pd/C catalyst for the synthesis of MF from fructose.^[17] Chidambaram and Bell reported a two-step approach for the catalytic conversion of glucose to DMF with a Pd/C catalyst in ILs, which gave a maxi-

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mum 47% conversion of glucose with 32% DMF selectivity.^[20] However, a potential drawback of this method was that the IL decreased the solubility of H₂. Hence, a high pressure of H₂ (6.2 MPa) was required, which made the process energy intensive. Under similar reaction conditions, the Ru/C catalyst failed to produce DMF from HMF.^[20] Thananatthanachon and Rauchfuss reported a effectiveness of the Pd/C catalyst for the onepot conversion of fructose to DMF with a maximum 51% overall DMF yield.^[21]

Herein, we report the effectiveness of the Ru/C catalyst for the conversion of fructose and biomass into DMF. Our strategy is to execute the multistep DMF synthesis from an HMF platform^[22] in a single vessel. We used formic acid (FA) as a H₂ source and a deoxygenating agent. The IL [DMA]⁺[CH₃SO₃]⁻ (DMA = *N*,*N*-dimethylacetamide) was found to be effective for the hydrolysis and dehydration of untreated biomass into HMF in the first step of the sequential transformation. To address the sustainability issue, we used inexpensive and readily available lignocellulosic biomass substrates, for example, sugarcane bagasse and agar.

Results and Discussion

The Ru/C catalyst has long been known for its effectiveness in the hydrogenolysis of polyols to alkanes.^[23, 24] In all cases, the active carbon support acts as a binder for the facile hydrogenation. The weak Ru-C(support) interaction in the catalyst can also greatly influence the reactivity of the Ru species. As discussed above, the active carbon-supported Pd catalyst showed moderate activity in the preparation of DMF from fructose,^[21] however, the Ru/C catalyst was ineffective in producing DMF from HMF in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) under H_2 (6.2 MPa).^[20] To examine the catalytic effectiveness of Ru/C in the presence of a sustainable hydrogen storage agent, FA, the present DMF synthesis from biomass and biomass-derived carbohydrate has been investigated under mild conditions. The Ru/C catalyst with 5 wt% Ru loading was prepared by ultrasonicating a RuCl₃·3H₂O and activated charcoal mixture followed by the reduction of the metal precursor with NaBH₄ (see the Experimental Section). Characterization of the Ru/C catalyst by means of powder XRD and high-resolution TEM (HRTEM, Figures S1 and S2 in the Supporting Information) showed the presence of metallic Ru on the activated carbon surface. Preliminary experiments to study the effectiveness of the Ru/C catalyst for the one-pot transformation of HMF to DMF were performed in the presence of FA as a hydrogen source and a catalytic amount of concentrated H₂SO₄. The ¹H NMR spectrum of the product solution using mesitylene as an internal standard revealed the formation of 37% DMF along with 43% 5-(formyloxymethyl)furfural (FMF) intermediate, 12% unconverted HMF, and 3% levulinic acid (LA, Figure S3). LA is the rehydration product of HMF with water. The formation of DMTHF and MF was not evidenced under our mild reaction conditions, as observed under high-pressure conditions (2.1 MPa H₂) for the conversion of fructose with RuCl₃ and Pd/ C catalysts.^[17-19] The catalytic transformation of HMF to DMF takes place by the hydrogenation of HMF to bis(hydroxymethyl)furan (BHMF) followed by the hydrogenolysis of BHMF to DMF. In an earlier report, the synthesis of BHMF from fructose was carried out by using a Pd/C catalyst and FA as a hydrogen source.^[20] In the present study, the hydrogenation-hydrogenolysis steps were performed using the Ru/C catalyst in the presence of two equivalents of FA and a catalytic amount of concentrated H₂SO₄. Detailed reaction conditions and yields of DMF from various substrates are summarized in Table 1. In the case of fructose, 30% DMF was obtained from a reaction conducted with oil-bath heating (Table 1, entry 1). In addition, 32% HMF intermediate, 20% FMF intermediate, and 12% LA were also present in the product solution as identified from the ¹H NMR spectrum (Figure S4). Based on quantified DMF, unconverted intermediates, and LA, the total conversion of fructose can be calculated to be 94%. As microwave (MW)-assisted biomass transformation has been effective for selective conversions to HMF,^[25,26] the present one-pot transformation of fructose to DMF was also carried out under MW-assisted heating. The first step involved the synthesis of HMF in the presence of FA as a dehydration catalyst at 150°C for 10 min. In a consecutive step, the intermediate HMF was converted to DMF by hydrogenation and hydrogenolysis reactions using the Ru/C catalyst at 75 °C for 45 min in THF. The reaction produced a maximum yield of 32% DMF (Table 1, entry 2). A comparative analysis of the results shown in entries 1 and 2 of Table 1 revealed that the MW-assisted heating experiment produced 32% DMF in 55 min as compared to 30% DMF in 17 h with oilbath heating. The ¹H NMR spectra revealed that the transformation of HMF to DMF occurred via the formation of FMF as an intermediate. The ¹H NMR spectra of the reaction mixture showed one singlet at $\delta = 9.65$ ppm corresponding to the –CHO proton and two doublets at δ = 7.21 and 6.61 ppm corresponding to the furan ring protons of FMF (Figures S5 and S6). The formyloxy functionalization of the --CH₂OH group of HMF (Scheme 1) led to the formation of FMF before the addi-



Scheme 1. Formation of FMF intermediate during DMF synthesis.

tion of Ru/C catalyst and H_2SO_4 . In the presence of Ru/C, FA, and H_2SO_4 , the sequential hydrogenation and hydrogenolysis reactions occurred and DMF was obtained as the desired product.

This one-pot DMF synthesis was extended to α -cellulose. As shown in Table 1, the Brønsted-acidic IL [DMA]⁺[CH₃SO₃]⁻ was used as a catalyst in the first step for the conversion of α -cellulose into HMF in a DMA/LiCl solvent at 150 °C under oil-bath heating. In the second step, FA was added for the formylation of HMF. In the third step of this one-pot reaction, FMF was converted into the desired product, DMF, in the presence of Ru/C and a catalytic amount of H₂SO₄. The yield of DMF from

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Table 1. DMF preparation from different substrates.												
Entry	Substrate	Amount [g]	Step 1 reagent	7 [°C]	<i>t</i> [min]	Step 2 reagent	7 [°C]	<i>t</i> [min]	Step 3 reagent	T [°C]	t [min]	DMF yield [g] ([%]) ^[a]
1	fructose	0.72	FA (2 mL)	150	120	Ru/C (0.8 g) H ₂ SO ₄ (28 μL) THF (8 mL)	75	900	-	-	-	0.116 (30)
2 (MI ^[b])	fructose	0.18	FA (0.5 mL)	150	10	Ru/C (0.2 g) H ₂ SO ₄ (8 μL) THF (2 mL)	75	45	-	-	-	0.031 (32)
3	α -cellulose	0.65	[DMA] ⁺ [CH ₃ SO ₃] ⁻ (0.065 g) DMA/LiCl (6.5 g)	150	60	FA (0.8 mL)	150	60	Ru/C (0.4 g) H ₂ SO ₄ (14 μL) THF (6 mL)	75	900	0.054 (14)
4 (MI ^[b])	α -cellulose	0.12	[DMA] ⁺ [CH ₃ SO ₃] ⁻ (0.012 g) DMA/LiCl (1.2 g)	150	10	FA (0.2 mL)	150	5	Ru/C (0.1 g) H₂SO₄ (3 μL) THF (1.5 mL)	75	45	0.011 (16)
5	sugarcane bagasse	0.50	[DMA] ⁺ [CH ₃ SO ₃] ⁻ (0.05 g) DMA/LiCl (8.0 g)	150	60	FA (1.0 mL)	150	60	Ru/C (0.4 g) H ₂ SO ₄ (14 μL) THF (6 mL)	75	900	0.049
6 (MI ^[b])	sugarcane bagasse	0.10	[DMA] ⁺ [CH₃SO₃] [−] (0.01 g) DMA/LiCl (1.5 g)	150	10	FA (0.25 mL)	150	5	Ru/C (0.1 g) H ₂ SO ₄ (4 μL) THF (1.5 mL)	75	45	0.011
7	agar	1.00	[DMA] ⁺ [CH ₃ SO ₃] ⁻ (0.1 g) DMA/LiCl (6.0 g)	150	60	FA (2.0 mL)	150	60	Ru/C (0.8 g) H ₂ SO ₄ (35 μL) THF (10 ml.)	75	900	0.143 (24)
8 (MI ^[b])	agar	0.15	[DMA] ⁺ [CH ₃ SO ₃] ⁻ (0.015 g) DMA/LiCl (1.0 g)	150	10	FA (0.4 mL)	150	5	Ru/C (0.2 g) H ₂ SO ₄ (5 μL) THF (1.2 mL)	75	45	0.024 (27)
[a] GC analysis. DMF molar percentage was calculated with respect to the starting substrates. [b] Irradiation at 300 W.												

 α -cellulose was 14% over 17 h (Table 1, entry 3). The total conversion of α -cellulose after the first step was 39% with the formation of 18% total reducing sugar, as determined by the phenol-H₂SO₄ method.^[27] In addition to DMF, unconverted HMF and FMF intermediates may also be present in the final crude product as observed in the conversion of a pure HMF sample. The conversion of α -cellulose under MW-assisted heating produced 16% DMF in a total reaction time of 1 h (Table 1, entry 4). The yield of DMF from α -cellulose is significantly lower than that obtained from fructose, which could be due to the robust crystalline structure of α -cellulose, which consists of a 3D network of hydrogen bonding interactions.^[6,28] Therefore, the degradation of cellulose into hexose units was carried out with a strongly acidic IL catalyst, [DMA]⁺[CH₃SO₃]⁻. Our previous study has shown that the maximum yield of HMF from α cellulose was 29% when using the [DMA]⁺[CH₃SO₃]⁻ catalyst.^[29] Nevertheless, α -cellulose is a new biorenewable substrate capable of producing DMF under the present reaction conditions.

The substrate scope of this method for the one-pot synthesis of DMF was extended to sugarcane bagasse and agar. As shown in Table 1, both oil-bath and MW-assisted heating experiments were performed to compare the DMF yields. In the case of sugarcane bagasse, $[DMA]^+[CH_3SO_3]^-$ was used for the in situ conversion of this untreated biomass into HMF at 150 °C for 1 h under oil-bath heating. In the second step, FA was added for the formylation of the HMF intermediate. In the subsequent step, Ru/C, $H_2SO_{4\nu}$ and THF were added to facilitate the hydrogenation–hydrogenolysis of HMF to produce the product, DMF. The oil-bath and MW-assisted heating experiments produced 0.049 and 0.011 g of DMF from 0.5 and 0.1 g of starting sugarcane bagasse in 17 and 1 h, respectively (Table 1, entries 5 and 6). This result shows that the Ru/C catalyst is guite effective considering that sugarcane bagasse contains only 25% hemicellullose, 50% cellulose (i.e., a total of about 75% carbohydrate), and 25% lignin.^[30] The conversion of cellulose to HMF is more difficult than that of hemicellulose due to the difference in their microcrystalline structures, which makes cellulose more resistant to hydrolysis than hemicelluloses.^[31] In the oil-bath heating experiment, the total conversion of sugarcane bagasse after the first reaction step was 52% with the formation of 20% total reducing sugar as determined by using the phenol-H₂SO₄ method.^[27] A ¹³C NMR investigation of the reaction products of the second reaction step of sugarcane bagasse conversion confirmed the formation of FMF from its characteristic signals at $\delta\!=\!$ 178.0 and 160.1 ppm corresponding to -OCHO and -CHO groups, respectively (Figure 1 a). Figure 1 b shows the ¹³C NMR spectra of the final DMF product along with some unconverted FMF intermediate. In this process, the use of FA as a hydrogen source as well as a deoxygenating agent enabled the three-step reaction to be performed in one pot. The amount of FA (0.8-1.0 mL) required for the conversion of cellulose and sugarcane bagasse substrates was less than that used for the fructose conversion (2 mL). This is because the role of FA in the conversion of cellulose and sugarcane bagasse substrates was limited to formyloxy ester (-CH₂OCHO) formation, whereas in the case of fructose conversion, FA also acted as a dehydration catalyst for HMF formation in the first step. Due to the robust crystalline structure of α -cellulose with its 3D network of hydrogen bond-

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Figure 1. a) ¹³C NMR (CDCl₃) spectrum of the reaction mixture showing FMF intermediate during the progression of a reaction between sugarcane bagasse and [DMA]⁺[CH₃SO₃]⁻ catalyst in DMA/LiCl (10 wt %) and subsequent heating with FA. b) ¹³C NMR spectrum (CDCl₃) of the final oily product obtained from sugarcane bagasse as a starting substrate.

ing interactions,^[6,28] the [DMA]⁺[CH₃SO₃]⁻ catalyst was used for hydrolysis and subsequent dehydration of cellulose and sugarcane bagasse substrates into HMF. We found that FA was ineffective for in situ HMF formation from cellulose and sugarcane bagasse. In both reactions, ¹H and ¹³C NMR spectra of the reaction mixture revealed the formation of FMF intermediate after the addition of FA. In the presence of the Ru/C catalyst, FA acted as a hydrogen source for the hydrogenation of the –CHO group of HMF (Step 1 in Scheme 2) to form intermedi-





ate **A**. The subsequent deoxygenation of intermediate **A** by the Ru/C catalyst led to the formation of intermediate **B**. The final product, DMF, was formed via the formyloxy ester (intermediate **C**) of intermediate **B** in the presence of FA and H_2SO_4 followed by another deoxygenation step in the presence of the Ru/C catalyst. Scheme 2 summarizes the formylation, hydrogenation, and hydrogenolysis steps discussed above.

Thananatthanachon and Rauchfuss reported that the Pd/C-FA catalytic system afforded overall 51% DMF from fructose.^[21] Chidambaram and Bell attempted HMF conversion with the Ru/C catalyst in [EMIM]Cl under 6.2 MPa H₂. DMF was not detected in the final product mixture.^[20] We found that carbonsupported, highly dispersed Ru nanoparticles of 5–8 nm are quite effective for DMF synthesis, giving a maximum 32% DMF yield from fructose.

The facile conversion of macroalgal polymeric carbohydrates into biofuels is a promising area of research.^[32] The synthesis of DMF from macroalgae-derived agar using a suitable catalyst is a challenging goal. To overcome this challenge, we have tested the one-pot reaction for the conversion of macroalgaederived agar into DMF under oil-bath and MW-assisted heating. As described in the experimental section and summarized in Table 1, the [DMA]⁺[CH₃SO₃]⁻ catalyst was used for the conversion of agar into HMF. The subsequent additions of FA, Ru/ C, and H₂SO₄ in Steps 2 and 3 resulted in the formation of 24% DMF in 17 h under oil-bath heating (Scheme 3, Table 1,



Scheme 3. One-pot conversion of macroalgae-derived agar into DMF.

entry 7). The conversion of agar after the first reaction step was 67% with the formation of 23% total reducing sugar. In addition to DMF, unconverted HMF and FMF intermediates are also expected to be present in the final crude product in the same ratio as that observed for the conversion of pure HMF. The same reaction under MW-assisted heating produced 27% DMF in 1 h (Table 1, entry 8).

A previous report demonstrated the formation of a maximum 10% yield of HMF from agar powder using a solid Brønstedacidic Dowex 50WX8 catalyst in [EMIM]Cl.^[14] To improve the degradation of the polymeric unit present in agar, we have used the [DMA]⁺[CH₃SO₃]⁻ catalyst in the present study, which indeed accelerated the in situ HMF formation as evidenced from the 24% yield of DMF.

In addition to the broad substrate scope of the present onepot DMF synthesis combining the three steps, we have developed a synthesis method for the efficient conversion of HMF and inexpensive biomass to EMF, another promising biofuel, by using [DMA]⁺[CH₃SO₃]⁻ as an acid catalyst for the etherification of HMF in ethanol. We began with HMF (0.5 g) as a substrate, which was reacted with [DMA]⁺[CH₃SO₃]⁻ catalyst (0.05 g) in ethanol (10 mL) at 120 °C. As shown in Table 2

Table 2. EMF preparation from HMF and biomass substrates. ^[a]								
Entry	Substrate ([g])	[DMA] ⁺ [CH ₃ SO ₃] ⁻ [g]	EtOH [mL]	t [h]	Yield ^[b] [g] ([%])			
1	HMF (0.5)	0.05	10	15	0.56 (92)			
2	fructose (2.0)	0.20	20	16	1.09 (64)			
3	cellulose fibers (1.0)	0.20	15	20	0.21 (22)			
4	sugarcane bagasse (1.0)	0.20	15	20	0.28			
[a] Reaction conditions: $T = 120$ °C. [b] Isolated yield comprising EMF + EL in a 9:1 ratio.								

(entry 1), almost quantitative conversion of HMF was achieved in 15 h under oil-bath heating. The oily liquid product was purified by using column chromatography. The isolated yield of purified product was 0.56 g. Analysis of the isolated product by means of ¹H and ¹³C NMR spectroscopy revealed the formation of EMF in a 9:1 ratio with ethyl levulinate (EL). $^{\scriptscriptstyle [33]}$ The ratio of EMF to EL in the isolated product was determined by comparing the signal intensities of the -OCH₂CH₃ peaks. The reasons for the simultaneous formation of EMF and EL could be 1) catalysis of the ring-opening of EMF by the Brønsted-acidic [DMA]⁺[CH₃SO₃]⁻ catalyst and 2) esterification of LA, which was formed as a byproduct from the rehydration of HMF. The present one-pot synthesis of EMF from biomass refrained from the use of toxic CrCl₂^[14] and concentrated HCl^[10] used in previously reported methods. A recent study reported the formation of EL as a major product from the conversion of a series of substrates including HMF, fructose, and glucose over 22 h in the presence of sulfonic-functionalized IL catalyst.^[15] However, the same reaction produced EMF as the major product when carried out for 2 h. In the present study, EMF was obtained as a major product from the reaction between [DMA]⁺[CH₃SO₃]⁻ and HMF, suggesting that the acid strength of the catalyst was enough for the complete etherification of HMF in ethanol and hence that the LA formation, esterification of which led to EL, was minimal.

The effectiveness of the $[DMA]^+[CH_3SO_3]^-$ catalyst was further investigated for the synthesis of EMF from fructose, cellulose fibers, and inexpensive biomass waste, sugarcane bagasse, at 120 °C under oil-bath heating. A reaction between fructose (2.0 g) and $[DMA]^+[CH_3SO_3]^-$ (0.2 g) in ethanol for 16 h gave 1.09 g isolated product (Table 2, entry 2).

¹H NMR spectral data of the purified product revealed the complete conversion of the in situ-formed HMF into a mixture of EMF and EL in a 9:1 ratio (Figures S11 and S12). In the case of cellulose, a reaction between cellulose fibers (1.0 g) and $[DMA]^+[CH_3SO_3]^-$ (0.2 g) in ethanol at 120 °C produced 0.21 g isolated oily product in 20 h (Table 2, entry 3). The progression of the reaction was monitored by the appearance and disappearance of the proton signal of the –CHO group of the intermediate HMF. The results again showed the complete conversion of in situ-generated HMF into a mixture of EL and EMF. The $[DMA]^+[CH_3SO_3]^-$ catalyst was also effective for the conversion of sugarcane bagasse into EMF in ethanol. The one-pot reaction between $[DMA]^+[CH_3SO_3]^-$ (0.2 g) and sugarcane bagasse (1.0 g) at 120 °C gave 0.28 g isolated oily product contain-

ing a mixture of EMF and EL in a 9:1 ratio (Table 2, entry 4). A comparative analysis of the results shown in Table 2 revealed that the reaction with sugarcane bagasse produced more EMF than that with cellulose fibers under identical reaction conditions. We have also investigated the formation of EMF as a function of reaction time by monitoring the progression of the reaction by using ¹H NMR spectroscopy. ¹H NMR spectra of the reaction mixture were recorded at regular time intervals in the presence of mesitylene as an internal standard. The yield of the products (EMF+EL) was determined by comparing the signal intensity of the –CHO proton (δ = 9.59 ppm) of EMF with that of the mesitylene aromatic ring proton at $\delta =$ 6.78 ppm. The yield of HMF was recorded as a function of reaction time for all substrates. The results plotted in Figure 2 reveal that HMF is a preferred substrate for the quantitative conversion to EMF with 90% selectivity, whereas the strong 3D network of H bonds^[6] in the structure of cellulose precludes its facile hydrolysis.



Figure 2. EMF formation curves as a function of reaction time (h) for different substrates catalyzed by $[DMA]^+[CH_3SO_3]^-$ in ethanol.

Conclusions

We have described the one-pot synthesis of promising biofuels, 2,5-dimethylfuran (DMF) and 5-ethoxymethylfurfural (EMF), from a range of readily available biomass substrates. The first step of the one-pot reaction involved in situ 5-hydroxyemthylfurfural (HMF) synthesis using formic acid (FA) as a catalyst for fructose and the $[DMA]^+[CH_3SO_3]^-$ (DMA = N,N-dimethylacetamide) catalyst for cellulose and untreated biomass. In the subsequent steps, HMF was transformed into DMF by hydrogenation and hydrogenolysis reactions using FA and Ru/ C. We found that the Ru/C catalyst is quite effective, giving a maximum yield of 32% DMF from fructose and 27% from agar. We have identified 5-(formyloxymethyl)furfural as an intermediate during the reactions by means of ¹H and ¹³C NMR spectroscopy. The Brønsted-acidic IL catalyst, [DMA]⁺[CH₃SO₃]⁻, was also effective for the clean synthesis of 5-ethoxymethylfurfural (EMF), another potential biofuel, from HMF, fructose, sugarcane bagasse, and agar in ethanol. Under mild reaction conditions, HMF was guantitatively converted to EMF with high selectively. Investigations are underway to examine the effective-

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ness of new catalysts (e.g., bimetallic carbon or clay-supported catalysts) and hydrogen sources for the efficient hydrogenation-hydrogenolysis of HMF to DMF.

Experimental Section

Materials

p-Fructose, α -cellulose, 2,5-dimethylfuran, formic acid, and activated carbon were purchased from Sigma–Aldrich. RuCl₃·3H₂O and agar powder were obtained from SRL, India. DMA, THF, diethyl ether, and LiCl were purchased from Spectrochem, India. Sugarcane bagasse was collected from a local sugarcane juice shop. Cellulose and sugarcane bagasse were oven-dried to constant weight at 80 °C prior to use.

Characterization

HRTEM images of Ru/C were recorded by using a TECNAI G2T30, u-TWIN instrument with a tungsten filament as the electron source. Powder XRD data for Ru/C were collected by using a Rigaku Miniflex 2 instrument. Conversions of D-fructose, cellulose, and sugarcane bagasse to DMF under MW-assisted heating were performed by using a CEM Matthews WC Discover microwave reactor, model no. 908010 DV9068, equipped with programmable pressure and temperature controller. ¹H and ¹³C NMR spectra were collected by using a JEOL JNM ECX-400 P 400 MHz instrument, and data were processed by using the JEOL DELTA program, version 4.3.6. DMF yields were measured by using a Shimadzu GC-2014 chromatograph equipped with a flame ionization detector (FID) detector. Conversions of α -cellulose, sugarcane bagasse, and agar substrates during DMF synthesis were determined by the change of substrate weight before and after the first step of the reaction.

Preparation of Ru/C

RuCl₃·3 H₂O (130 mg) and activated charcoal (1.0 g, 100 mesh size) were added to a mixture of THF and H₂O (100 mL, 1:1, v/v). After the mixture was ultrasonicated for 1 h and mechanically stirred for another 10 h, a solution (10 mL) containing an equivalent amount of NaBH₄ and Na₂CO₃ with respect to RuCl₃·3 H₂O was added dropwise, and the mixture was stirred for 1 h at 10 °C. The material was collected by filtration, washed with distilled water and ethanol, and dried in a vacuum oven at 60 °C.

Preparation of DMF under oil-bath heating

Preparation of DMF from fructose: Fructose (0.72 g) and FA (2.0 mL) were mixed in a round-bottomed flask and heated to reflux with continuous stirring at 150 °C for 2 h. The resulting dark solution was cooled to room temperature and diluted with THF (8 mL). A catalytic amount of concentrated H_2SO_4 (28 μ L) and Ru/C (0.8 g) were then added to the dark solution. The mixture was heated to reflux at 75 °C for an additional 15 h. After cooling the solution to room temperature, the Ru/C catalyst was separated by filtration. The filtrate containing the desired product was mixed with H_2O (5 mL). The organic phase was extracted into diethyl ether (3×5 mL). A crude product containing a mixture of DMF, unconverted HMF, and FMF intermediates and LA was obtained after removing THF and diethyl ether by vacuum distillation at 80 °C.

CDCl₃): δ = 2.24 (s, 6H, 2CH₃), 5.82 ppm (s, 2H, CH); ¹³C NMR (100 Hz, CDCl₃): δ = 13.45 (CH₃), 105.91 (CH), 150.15 ppm (CH).

Preparation of DMF from α -cellulose: α -Cellulose (0.65 g) and [DMA]⁺[CH₃SO₃]⁻ (0.065 g) were mixed with DMA/LiCl (6.5 g) in a round-bottomed flask. The reaction mixture was heated to reflux with continuous stirring at 150 °C for 1 h. After 1 h, FA (0.8 mL) was added, and the mixture was heated to reflux for another 1 h at 150 °C. The resulting dark solution was cooled to room temperature and diluted with THF (6 mL). After adding a catalytic amount of H₂SO₄ (14 µL) and Ru/C (0.4 g) to the resulting solution, the mixture was heated to reflux at 75 °C for 15 h. After completion of the reaction, the Ru/C catalyst was recovered by filtration. The filtrate was diluted with H₂O (5 mL), and the organic layer was extracted into diethyl ether. The product was obtained from the organic layer after removing THF and diethyl ether by vacuum distillation at 80 °C.

Preparation of DMF from sugarcane bagasse: Sugarcane bagasse (0.50 g) and [DMA]⁺[CH₃SO₃]⁻ (0.050 g) were mixed with DMA/LiCl (8.0 g) in a round-bottomed flask. The reaction mixture was heated to reflux with continuous stirring at 150 °C for 1 h. FA (1.0 mL) was added, and heating was continued for another 1 h at 150 °C. The mixture was cooled to room temperature, and unreacted sugarcane bagasse was removed from the solution by filtration. The filtrate was mixed with THF (6 mL), concentrated H₂SO₄ (14 μ L), and Ru/C (0.4 g). The resulting solution was heated to reflux with continuous stirring at 75 °C for 15 h. After completion of the reaction, the Ru/C catalyst was recovered by filtration. The filtrate was diluted with H₂O (4 mL), and the organic layer was extracted into diethyl ether. The desired product was obtained from the organic layer after removing THF and diethyl ether by vacuum distillation at 80 °C.

Preparation of DMF from agar: $[DMA]^+[CH_3SO_3]^-$ and agar powder (1.0 g) (1.0 g) were mixed with DMA/LiCl (6 g) in a round-bottomed flask. The reaction mixture was heated to reflux at 150 °C for 1 h. FA (2.0 mL) was added and stirring was continued for 1 h at 150 °C. The mixture was cooled to room temperature, and unreacted agar was removed by filtration. The filtrate was mixed with THF (10 mL), concentrated H₂SO₄ (35 µL) and Ru/C (0.8 g) and heated to reflux at 75 °C for 15 h. The desired product was extracted as described in the preparation from sugarcane bagasse.

Preparation of DMF from HMF: A suspension of HMF (0.1 g), FA (0.31 mL), H_2SO_4 (6 μ L), THF (4 mL), and Ru/C (0.16 g) was heated to reflux at 75 °C with continuous stirring for 15 h. After cooling the solution to room temperature, the Ru/C was separated by filtration, and the filtrate was mixed with H_2O (1 mL). The organic phase was extracted into diethyl ether. A crude product containing a mixture of DMF, unconverted HMF, FMF intermediate, and LA was obtained after removing THF and diethyl ether by vacuum distillation at 80 °C.

Preparation of DMF under microwave-assisted heating

Preparation of DMF from fructose: A MW tube was charged with fructose (0.18 g) and FA (0.5 mL). The loaded tube was inserted into the MW reactor preset at 150 °C for 10 min. After 10 min, THF (2 mL), concentrated H₂SO₄ (8 μ L), and Ru/C (0.2 g) were added, and the reaction was continued under MW irradiation at 75 °C for 45 min. The reaction mixture was cooled to room temperature, and the solid catalyst was removed by filtration. The filtrate was diluted with H₂O (3 mL), and the organic layer was extracted into diethyl ether. The desired product was obtained from the organic

layer after removing THF and diethyl ether by vacuum distillation at 80 $^\circ\text{C}.$

Preparation of DMF from α -cellulose: [DMA]⁺[CH₃SO₃]⁻ (0.012 g), α -Cellulose (0.12 g), and DMA/LiCl (1.2 g) were loaded into a MW tube. The loaded tube was inserted into the MW reactor preset at 150 °C for 10 min. After 10 min, FA (0.2 mL) was added, and the reaction was continued for another 5 min at the same temperature. To the resulting dark solution, THF (1.5 mL), concentrated H₂SO₄ (3 μ L), and Ru/C (0.1 g) were added, and the reaction was continued under MW irradiation at 75 °C for 45 min. The desired product was extracted as described in the preparation from fructose.

Preparation of DMF from sugarcane bagasse: Sugarcane bagasse (0.10 g), [DMA]⁺[CH₃SO₃]⁻ (0.01 g), and DMA/LiCl (1.5 g) were loaded into a MW tube. The loaded tube was inserted into the MW reactor preset at 150 °C for 10 min. After 10 min, FA (0.25 mL) was added, and the reaction was continued for another 5 min at the same temperature. The mixture was cooled to room temperature, and unreacted sugarcane bagasse was removed by filtration. The filtrate was mixed with THF (1.5 mL), a catalytic amount of concentrated H₂SO₄ (4 μ L) and Ru/C (0.1 g), and the reaction was continued under MW irradiation at 75 °C for another 45 min. The desired product was extracted as described in the preparation from fructose.

Preparation of DMF from agar: $[DMA]^+[CH_3SO_3]^-$ (0.015 g), agar powder (0.15 g), and DMA/LiCl (1 g) were loaded into a MW tube. The loaded tube was then inserted into the MW reactor preset at 150 °C for 10 min. After 10 min, FA (0.4 mL) was added, and the reaction was continued for another 5 min at the same temperature. The mixture was cooled to room temperature, and unreacted agar was removed by filtration. The filtrate was mixed with THF (1.2 mL), a catalytic amount of concentrated H₂SO₄ (5 µL) and Ru/C (0.2 g), and the reaction was continued under MW irradiation at 75 °C for another 45 min. The desired product was extracted as described for the preparation from fructose.

Preparation of EMF

Preparation of EMF from HMF: The synthesis of EMF from HMF was carried out in a 100 mL round-bottomed flask under oil-bath heating. The flask was charged with HMF (0.5 g), [DMA]⁺[CH₃SO₃]⁻ (0.05 g), and ethanol (10 mL) and heated to reflux with continuous stirring at 120°C for 15 h. The reaction mixture was cooled to room temperature, ethanol was evaporated under vacuum, and the oily residue was column chromatographed with a silica gel (200-400 mesh) as the stationary phase and a mixed dichloromethane/diethyl ether solvent (2:1, v/v) as the mobile phase. After separating [DMA]⁺[CH₃SO₃]⁻, the oily liquid product was characterized by means of ¹H and ¹³C NMR spectroscopy. The total isolated yield was 0.56 g. A comparison of the signal intensities of the -CH₂OEt group confirmed the presence of EMF and EL in the isolated product in a 9:1 ratio. EMF: ¹H NMR (400 Hz, CDCl₃): $\delta = 9.59$ (s, 1 H), 7.19 (d, J=2.8 Hz, 1 H), 6.50 (d, J=2.8 Hz, 1 H), 4.53 (s, 2 H), 3.69 (q, 2 H), 1.20 ppm (t, 3 H); 13 C NMR (100 Hz, CDCl₃): δ = 14.98, 64.67, 66.58, 111.01, 122.3, 152.22, 160.88, 177.79 ppm. EL: ¹H NMR (400 MHZ, CDCl_3): δ = 4.02 (q, 2 H), 2.72 (t, 3 H), 2.48 (t, 2 H), 2.14 (s, 3H), 1.20 ppm (t, 3H).

Preparation of EMF from fructose: Fructose (2.0 g) was dissolved in ethanol (20 mL) in a 100 mL round-bottomed flask. To this was added [DMA]⁺[CH₃SO₃]⁻ (0.20 g), and the solution was heated to reflux with continuous stirring at 120 °C for 16 h. The oily liquid

product was isolated and characterized as described in the preparation from $\ensuremath{\mathsf{HMF}}$.

Preparation of EMF from cellulose: Cellulose fibers (1.0 g) were suspended in ethanol (15 mL) in a 100 mL round-bottomed flask. To this was added [DMA]⁺[CH₃SO₃]⁻ (0.20 g), and the reaction mixture was heated to reflux with continuous stirring at 120 °C for 20 h. The oily liquid product was isolated and characterized as described in the preparation from HMF.

Preparation of EMF from sugarcane bagasse: Sugarcane bagasse (1.0 g) was suspended in ethanol (15 mL) in a 100 mL round-bottomed flask. To this was added $[DMA]^+[CH_3SO_3]^-$ (0.20 g), and the reaction mixture was heated to reflux with continuous stirring at 120 °C for 20 h. The oily liquid product was isolated and characterized as described in the preparation from HMF.

Determination of DMF yield

The yield of DMF was measured by using a GC (Shimadzu GC-2014) equipped with a FID detector and Zebron (ZB-35) capillary column (0.32 mm, inner diameter 0.25 μ m × 30 m). Essential parameters of the GC analysis were as follows: Injection volume 1.0 μ L, inlet temperature 270 °C, detector temperature 300 °C, and a split ratio of 1:100. The initial column temperature of 50 °C (2 min) was increased with temperature ramp of 10 °C min⁻¹ to the final temperature of 280 °C. The diethyl ether extractant of the reaction mixture was diluted with methanol for the GC run. DMF was identified by using its retention time in comparison to an authentic sample. The peak of the gas chromatogram was integrated, and the actual concentration of each component was obtained from the precalibrated plot of peak area against concentration.

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FULL PAPERS

Biomass breakdown in one pot: The one-pot conversion of lignocellulosic and algal biomass into liquid fuel, 2,5dimethylfuran, has been achieved by using a multicomponent catalytic system comprising [DMA]⁺[CH₃SO₃]⁻ (DMA = N,N-dimethylacetamide), Ru/C, and formic acid. A reaction route has been elucidated based on ¹H and ¹³C NMR spectroscopic data. Another promising biofuel has also been synthesized by using [DMA]⁺[CH₃SO₃]⁻ as catalyst.



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One-Pot Conversions of Lignocellulosic and Algal Biomass into Liquid Fuels