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One-Step Catalytic Transformation of Carbohydrates and Cellulosic Biomass to 2,5-Dimethyltetrahydrofuran for Liquid Fuels

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Existing technologies to produce liquid fuels from biomass are typically energy-intensive, multistep processes. Many of these processes use edible biomass as starting material. Carbohydrates, such as mono- and polysaccharides and cellulose, typically constitute 50–80% of plant biomass. Herein, we report that hexose from a wide range of biomass-derived carbohydrates, cellulose, and even raw lignocellulose (e.g., corn stover) can be converted into 2,5-dimethyltetrahydrofuran (DMTHF) in one step, in good yields and under mild conditions in water. Under the same conditions, 2-methyltetrahydrofuran is formed from pentose. The reaction employs a soluble rhodium catalyst, dihydrogen, and HI/HCl + NaI. The catalytic system is robust and can be recycled repeatedly without loss of activity. DMTHF is superior to ethanol and has many of the desirable properties currently found in typical petroleum-derived transportation fuels.

Introduction

The production of liquid fuels directly from biomass is of great current interest, given the diminishing reserves of fossil fuels such as coal, oil, and natural gas—the current commercial sources of fuels.[1] Biomass is the only practical source of renewable liquid fuels.[2] Furthermore, the use of biomass substantially reduces net carbon dioxide emissions because the latter is recycled in biomass regeneration.

Existing technologies to produce liquid fuels from biomass are typically energy-intensive, multistep processes.[3] The principal commercial method employed to produce liquid fuels from biomass is the production of ethanol by fermentation of sugars. Unfortunately, this process often uses foodstuff, such as corn kernels, as a starting material;[4] however, efforts have also been made to produce ethanol from cellulose and nonfood biomass sources.[5] Ethanol is not a good candidate for liquid fuels because of its low energy density (23 $\mathrm{MJ\,L^{-1}}$), high volatility (bp 78 °C), and high solubility in water (fully miscible).[6] For these reasons researchers have tried to seek other liquid fuel candidates that can be produced from renewable biomass. Dumesic et al. have reported the two-step synthesis of 2,5-dimethylfuran (DMF) as liquid fuel via the platform chemical 5-hydroxymethylfurfural (HMF), which can be derived by the dehydration of fructose.[7] Compared to ethanol, DMF possesses a higher energy density (31.5 $\mathrm{MJ\,L^{-1}}$), lower volatility (bp 92–94 °C), and is immiscible with water. DMF is thus a better candidate for liquid fuel. However, the application of this process would be greatly limited if it would rely on fructose as the only source of HMF. Consequently, Zhang et al.[8a] and Ying et al.[9] have published high-yield conversions of both glucose and fructose into HMF in ionic-liquid solvents. Zhang et al.[8b] and Binder and Raines[10] have further improved this process by showing that even cellulose and lignocellulose can be converted to HMF in moderate yields. Finally, Mascal and Nikitin reported a high-yield conversion of cellulose and other raw biomass into 5-(chloromethyl)furfural, which can be subsequently converted into ethoxymethylfurfural or 5-methylfurfural for liquid fuel.[11] However, these processes involve multiple steps and sometimes require an additional separation step. Also, some of them employ relatively expensive ionic liquids as reaction media.

Jacoby has concluded that “Ideally, scientists would like to devise a simple, one-step or one-pot process that directly converts agricultural and municipal plant waste and other forms of raw biomass to valuable products.”[12] Accordingly, we have explored the possibility of a one-step transformation of biomass-derived carbohydrates, cellulose, and raw lignocellulose (e.g., corn stover) to 2,5-dimethyltetrahydrofuran (DMTHF) for liquid fuels. DMTHF is similar to DMF in terms of energy density (31.8 $\mathrm{MJ\,L^{-1}}$), volatility (bp 90–92 °C), and solubility (immiscible in water). However, because DMTHF is a saturated molecule it has good storage and transportation stability and is a better candidate for liquid fuel.

A multifunctional catalyst is required to produce DMTHF directly from cellulosic biomass, via hydrolysis, dehydration, and hydrogenation reactions. In our experiments, a homogeneous catalyst system composed of rhodium salt and an acid under hydrogen atmosphere was applied. Similar combinations of metal catalyst, acid, and hydrogenation have been examined for deoxygenation[13] and for glycerol[14] and sorbitol[15] transformations. However, we are unaware of any reported deoxygenation of C_5–C_6 sugars, cellulose, or raw biomass using such

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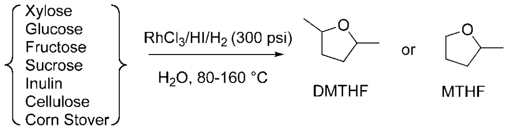
multifunctional catalysts. With our catalyst system, hexose from a variety of biomasses can be converted to DMTHF in one step in good yields under mild conditions in water; under the same conditions, 2-methyltetrahydrofuran (MTHF) is formed from pentose (Scheme 1). Carbohydrates, such as mono- and polysaccharides and cellulose, typically constitute 50–80 % of plant biomass.[16]



Scheme 1. One-step transformation of carbohydrates and cellulosic biomass to tetrahydrofuran derivatives (1 psi = 6.894×10^3 Pa).

Results and Discussion

Synthesis of DMTHF from fructose in biphasic solutions

In our search for appropriate reaction conditions, we began by using fructose in aqueous solution with HI and $RhCl_3{\cdot}xH_2O$ as catalysts under hydrogen (H_2) atmosphere (Table 1). At room temperature, no DMTHF was obtained. The conversion of fructose increased with temperature and at 80 °C, a 49 % yield of DMTHF was obtained (entry 2). Although the yield of DMTHF was around 50 %, the conversion of fructose was close to 100 % as indicated by ^{1}H NMR analysis of the aqueous layer. Neither the organic extractant (benzene was added after the reaction) nor the aqueous layer showed any other major product. However, a significant amount of insoluble carbonaceous material (humin) was found deposited at the end of the reaction, presumably owing to acid-catalyzed dehydration.[17] In fact, fructose was found to quantitatively convert to carbonaceous material by being heated at 80 °C for a few hours in the presence of HI, without $RhCl_3$ and H_2. We hypothesized that the yield of DMTHF could be further increased if an organic solvent was *pre-added* to extract the unstable reaction intermediates out of the aqueous layer before they decomposed further. Indeed, the addition of an organic solvent to the reaction system increased the yield of DMTHF dramatically, to around 75 % (entries 4–6). Benzene, toluene, and chlorobenzene could all be used as extracting solvents. Additionally, with an organic layer present, almost no humin (< 1 %) was formed during the reaction. DMTHF was very stable under these reaction conditions, and the reactions could be run overnight without any drop in the yield. The addition of NaCl to the aqueous layer to "salt out" the product did not improve the yield (entry 5).

The yield of DMTHF increased slightly by increasing the temperature and decreasing the amount of acid used (entries 7 and 8; the effect of acid amount on yield is shown in the Supporting Information). The highest yield of DMTHF from fructose was obtained at 140 °C with 1.2 mmol HI acid (81 %). Although yields of HMF from fructose as high as 92–96 % have been reported by using ionic liquids or *N,N*-dimethylacetamide (DMA) containing LiCl as solvent, a separation step (ca. 80 % yield) and hydrogenolysis step (ca. 50 % yield) were needed in order to get the final product (DMF for liquid fuels).[8–10] A larger-scale reaction was performed (10 mmol fructose) and an isolated yield of 68 % was achieved by distillation (entry 14).

Given that HI works well for the transformation, other protic acids such as HCl, HBr, and H_2SO_4 were also tested. Using HCl or HBr under conditions otherwise identical to entry 8, only 2–5 % DMTHF was obtained (entries 9 and 10). A large number of side products were observed in the organic (benzene) layer and a significant quantity of benzene was found to have been hydrogenated to cyclohexane. Thus, one of the functions of added iodide ion is to suppress unwanted side-reactions (see below). When H_2SO_4 was employed, no DMTHF and a large amount of humin were obtained (entry 11). Thus, HI provides the best result for this transformation. A catalyst loading 10 mol % was typically used; however, fairly good yields were obtained with loadings as low as 1 mol % (entries 12 and 13).

Table 1. One-step synthesis of DMTHF from fructose.[a]

Entry	$RhCl_3{\cdot}xH_2O$ [mmol]	Aq. fructose conc. [wt %]	*T* [°C]	*t* [h]	Acid [mmol]	Organic additive	DMTHF yield [%]
1	0.1	8	25	6	HI, 9	–	0
2	0.1	8	80	6	HI, 9	–	49
3	0.1	8	100	6	HI, 9	–	37
4	0.1	8	80	6	HI, 9	benzene	77
5[b]	0.1	8	80	6	HI, 9	benzene	69
6	0.1	8	80	6	HI, 9	toluene	74
7	0.1	6	120	4	HI, 1.5	toluene	79
8	0.1	6	140	2.5	HI, 1.2	C_6H_5Cl	81
9	0.1	6	140	2	HCl, 1.2	benzene	5
10	0.1	6	140	3	HBr, 1.2	benzene	2
11	0.1	6	140	2	H_2SO_4, 0.6	benzene	0
12	0.05	10	140	3	HI, 1.2	C_6H_5Cl	75
13	0.01	20	140	3	HI, 1.2	C_6H_5Cl	64
14[c]	1	10	140	6	HI, 7.7	C_6H_5Cl	76 (68)[d]

[a] 1 mmol fructose and 300 psi H_2 were used for entries 1–13. For entries 4–13, 4 mL of organic solvent was added prior to reaction. The yields of DMTHF were determined by ^{1}H NMR, using nitromethane as internal standard. [b] 0.6 g NaCl was added. [c] 10 mmol fructose, 1.8 g; 5 mL C_6H_5Cl; 300 psi H_2. [d] Isolated yield.

Separation of products and recycling of the catalyst

Two desirable aspects of any catalytic transformation are (1) the easy separation of products from the reaction mixture, and (2) the efficient recycling of the catalyst. One of the advantages of obtaining DMTHF directly and avoiding an HMF intermediate is that DMTHF is much less water-soluble than HMF and can be easily separated from aqueous reaction mixtures. Thus, DMTHF cleanly partitions into the organic extracting solvent at the end of the reaction. Of course, an additional distillation step would be necessary to isolate pure DMTHF. On the other hand, if DMTHF itself is the extractant, no further separation of the product is needed. Typically, the DMTHF obtained is a mixture of *cis* and *trans* isomers. Its identity was confirmed by ^{1}H NMR spectroscopy and by GC-MS. An ^{1}H NMR spectrum of the as-is benzene layer from Table 2, cycle 3 shows that the DMTHF isomers (in a ca. 9:1 ratio) are the only organic products present at detectable levels (Figure 1).

Table 2. Catalyst recycling in the conversion of fructose.[a]

Cycle	DMTHF yield [%]	Cycle	DMTHF yield [%]
1	77	6	75
2	86	7	86
3	81	8	82
4	78	9	79
5	81	10[b]	80

[a] Reaction conditions identical to Table 1, entry 4. The yield of DMTHF was determined by ^{1}H NMR spectroscopy, using nitromethane as internal standard. [b] The aqueous solution was filtered and the filtrate was used for cycle 10.

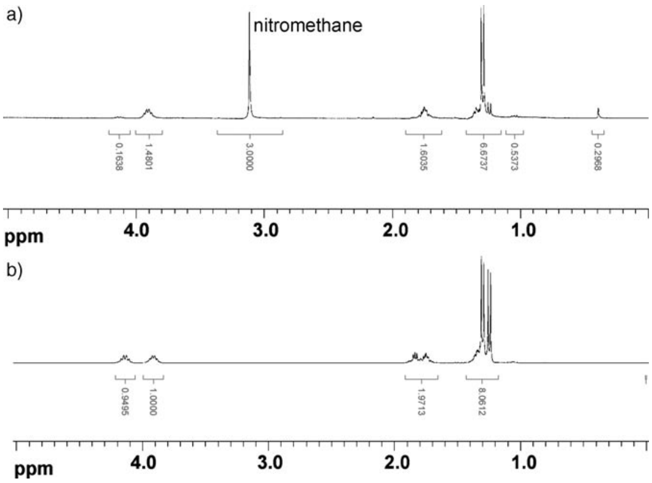


Figure 1. a) ^{1}H NMR spectrum of the as-is benzene layer from Table 2, cycle 3, versus b) ^{1}H NMR spectrum of a commercial mixture of DMTHF isomers (1:1) in benzene.

The catalyst left in the aqueous phase after product separation remains active. Fresh fructose can be added and the reaction can be continued. For example, after one reaction cycle and the removal of the benzene layer, 1 mmol fructose and 4 mL benzene were added back into the aqueous reaction mixture for the next cycle. The results of repeated cycling are summarized in Table 2. It is clear that the system remains active through at least 10 cycles without any attenuation in activity, suggesting the possibility of a continuous reactor system with counter-flows of the aqueous reaction mixture and the organic extractant. The small fluctuation of the yield is due to insufficient separation of organic and aqueous layers after each cycle. The actual catalyst is a water-soluble rhodium species, because there is no decrease in activity if the reaction mixture is filtered and the filtrate is used for the next cycle (cycle 10).

Synthesis of DMTHF from glucose

As anticipated,[18] glucose was found to be less reactive than fructose and required higher temperatures and longer reaction times (Table 3). At 80 °C, only a small amount of DMTHF was obtained from glucose. However, the yield of DMTHF increased dramatically upon raising the temperature and decreasing the amount of acid. With 1.5 equiv of HI at 140 °C, a 70% yield of DMTHF was obtained from glucose (entry 3). Further increasing temperature to 160 °C resulted in a slightly decreased yield of DMTHF and more humin formation.

Table 3. One-step synthesis of DMTHF from glucose.[a]

Entry	*T* [°C]	*t* [h]	HI [mmol]	DMTHF yield [%]
1	80	16	9	4
2	120	16	1.9	61
3	140	16	1.5	70
4	160	16	1.2	68
5	140	4	1.5	44
6	140	8	1.5	55

[a] Reaction conditions: 1 mmol glucose, 6 wt% in water; 300 psi H_2; 0.1 mmol $RhCl_3{\cdot}xH_2O$; 4 mL chlorobenzene.

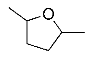
Conversion of other biomass-derived carbohydrates

The reaction conditions used for Table 3, entry 3 were also employed for a variety of other biomass-derived carbohydrates (Table 4). GC-MS analysis of the organic layer showed that in addition to the predominant product DMTHF (**1**), small amounts of other six-carbon products were also obtained from the reaction of hexose-based carbohydrates. These are 2,5-di-

Table 4. One-step transformation of carbohydrates into liquid fuels.[a]

Biomass/yield	DMTHF or MTHF [%]	**2** [%]	**3** [%]	**4** [%]	**5** [%]	Total [%]	Conversion[b] [%]
Fructose	81	0	4	1	1	87	100
Glucose	70	1	5	3	0	79	100
Inulin	73	0	5	0	1	79	96
Sucrose	82	0	4	0	0	86	96
Cellulose	54	4	6	1	0	65	90
Xylose	80	–	–	–	–	80	95

[a] Reaction conditions identical to Table 3, entry 3. The yields were determined by ^{1}H NMR and GC analysis, using nitromethane as internal standard. [b] Conversion based on the leftover carbohydrate in aqueous layer, using DMSO as internal standard.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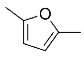
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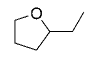
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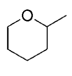
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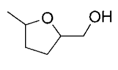
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methylfuran (**2**), 2-ethyltetrahydrofuran (**3**), 2-methyltetrahydropyran (**4**), and tetrahydro-5-methylfuran-2-methanol (**5**). No iodide-substituted products were observed. Only a trace amount of hydrogenation product from the solvent was observed. The observed side products are also potentially useful as liquid fuel additives.

Polysaccharides were hydrolyzed to the constituent glucose and fructose units under the acidic conditions employed. Thus, the conversions are based on the monomer units instead of the starting materials. Because of the somewhat lower reactivity of glucose, it was the only unreacted monomer observed at the end of the reaction. A very small amount of black carbonaceous material (<5% with cellulose, <1% with others) was also observed.

Fructose provided an 81% yield of DMTHF and an 87% combined yield of identified products; the corresponding numbers for glucose were 70% and 79%, respectively. Inulin comprises a group of naturally occurring polysaccharides produced by many types of plants, and mainly consists of fructose units with a terminal glucose.[19] It provided a 73% yield of DMTHF and a 79% combined yield of identified products. Sucrose (a disaccharide of glucose and fructose) formed DMTHF with yields comparable to that of fructose. A noteworthy conversion was that of the pentose, xylose, to 2-methyltetrahydrofuran (MTHF) with an 80% yield and without any other significant side product. This is the first example of the synthesis of MTHF from xylose in one step with such a high yield. MTHF is a major component in P-series oil.[20]

Synthesis of DMTHF from cellulose

Cellulose is a polysaccharide that consists of linear chains of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units. Because it is inexpensive and derived from nonfood resources, it is the most promising source for liquid fuels production. However, cellulose is insoluble in water and most organic solvents, and usually requires harsh processing conditions. Typical methods to produce HMF from cellulose by aqueous acid hydrolysis require high temperatures and pressures (250–400 °C, 10 MPa) and result in yields of less than 30%.[21] For the cellulose transformation shown in Table 4, the added cellulose initially formed an aqueous suspension; however, after the reaction the solution became clear. A 54% yield of DMTHF was obtained, which is higher than the yields reported for HMF from cellulose.[10,21,22] The combined yield of identified products was 65%.

In the course of our investigation to delineate the roles of acid and iodide ion in the reaction, we observed that it is possible to reduce the amount of acid if a high level of iodide ion is maintained (see Supporting Information). This allowed us to raise the reaction temperature without producing more humin (Table 5). A yield of DMTHF as high as 76% was obtained from glucose under the reaction conditions shown for entry 1. An isolated yield of 60% was obtained by distillation from a larger-scale reaction for glucose (10 mmol). The optimal conversion of cellulose required somewhat higher levels of acid and iodide ions. The highest yield of DMTHF obtained from cellulose was 76% (entry 4); the best result reported thus far. In addition, a 5% yield of 2-ethyltetrahydrofuran and a 2% yield of 2-methylpyran were obtained. Humin formation was minimal. A larger-scale (10×) reaction was run for cellulose transformation, resulting in a 63% isolated yield of DMTHF by distillation (entry 7).

Table 5. One-step synthesis of DMTHF from cellulose under less-acidic conditions.[a]

Entry	Biomass	HCl [mmol]	NaI [mmol]	T [°C]	t [h]	DMTHF yield [%]
1	Glucose	0.6	1.3	160	16	76
2[b]	Glucose	6	13	160	16	68 (60)[c]
3	Cellulose	0.9	1.3	160	18	54
4	Cellulose	0.6	2.0	160	18	75
5	Cellulose	0.9	2.0	160	16	76
6	Cellulose	0.9	2.0	160	6	67
7[d]	Cellulose	8	20	160	16	65 (63)[c,e]

[a] Reaction conditions: 1 mmol glucose, 10 wt% aq. solution; 0.16 g cellulose, 1 mmol glucose units in cellulose; 0.05 mmol $RhCl_3\cdot xH_2O$; 300 psi H_2; 1.8 mL water; 2 mL benzene. The yield of DMTHF was determined by ^1HNMR spectroscopy, using nitromethane as internal standard. [b] 10 mmol glucose, 1.8 g; 0.5 mmol $RhCl_3\cdot xH_2O$; 18 mL water; 5 mL chlorobenzene. [c] Isolated yield. [d] 1.6 g cellulose, 10 mmol of glucose units in cellulose; 0.5 mmol $RhCl_3\cdot xH_2O$; 18 mL water; 5 mL chlorobenzene. [e] Small amounts of **3** and **4** were present in the isolated DMTHF.

Production of liquid fuels from lignocellulosic biomass

Lignocellulose is the most abundant renewable biomass produced by photosynthesis. It consists primarily of plant cell wall material and is a complicated natural composite with three main biopolymers: cellulose, hemicellulose, and lignin.[23] The chemical inertness of lignocellulose is one of the primary impediments towards its application in a biorefinery. An expensive pretreatment process is usually required to produce fuels or chemicals from lignocellulosic biomass.[24] It would be most advantageous if it could be used directly without pretreatment.

We examined the conversion of crude corn stover by using reaction conditions optimized for cellulose, and the results are shown in Table 6. The reported yields are based on the glucan content (40.1%) and xylan content (24.1%) in corn stover. The yield from glucan were 41% for DMTHF, 6% for DMF, and 12% for 2,5-hexanedione, and that from xylan was 63% for MTHF; the highest yields reported to date. At the end of the reaction, around 15% humin was also formed, presumably from the lignin fraction of the corn stover.

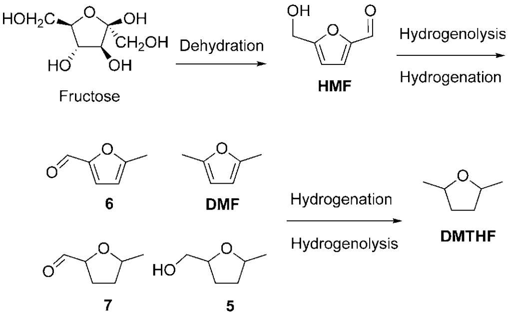
Table 6. Results for the conversion of untreated corn stover.[a]

Product	Yield [%]	Product	Yield [%]
DMTHF	41	**8**[b]	12
2	6	MTHF	63
3	3	Isolated[c]	0.29 g

[a] Reaction conditions identical to Table 5, entry 7. Yields based on ^{1}H NMR and GC analysis using nitromethane as internal standard. [b] **8**, 2,5-hexanedione. [c] The product isolated by distillation contains DMTHF, **2** and MTHF; combined theoretical yield 0.35 g.

Time course of the reaction

The one-step transformation from carbohydrates to DMTHF is proposed to go through a combination of hydrolysis, dehydration, hydrogenolysis, and hydrogenation reactions (Scheme 2).

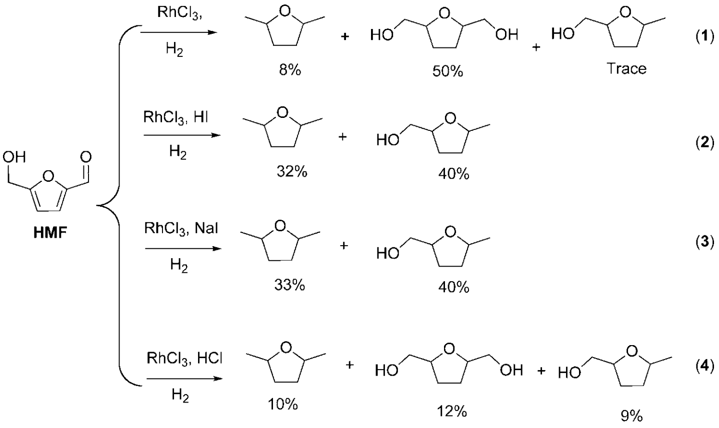


Scheme 2. Proposed reaction pathway from fructose to DMTHF.

To test this hypothesis, the reaction involving fructose was monitored as a function of time. When the reaction of fructose (conditions identical to Table 4, entry 1) was stopped after 10 min, a small amount of HMF was observed in the aqueous layer, along with significant quantities of unreacted fructose. In the organic layer, a mixture of DMTHF, DMF, 2-carbaldehyde-5-methyltetrahydrofuran (**7**), and **5** were observed (Scheme 2). HMF is known to be the major product from dehydration of fructose under acidic conditions. Only a small amount of HMF was observed owing to its expected instability under the reaction conditions. In a separate experiment, HMF was found to convert to a mixture of 5-methylfurfural (**6**) and DMF, together with a small amount of **7**, in 10 min under the same reaction conditions (Scheme 2). When the reaction of fructose was stopped after 30 min, a mixture of DMF and DMTHF, along with small amounts of **7** and **5**, was observed in the organic layer. A small amount of unreacted fructose was found in the aqueous layer. Finally, in 2 h, DMTHF was formed as the only major product, along with traces of side products as shown in Table 4, and no fructose was left in the aqueous layer.

Role of iodide in carbohydrate conversion

The iodide ion plays an important role in carbohydrate conversion. Because it is well-known that glucose and fructose can be dehydrated to form 5-hydroxymethylfurfural (HMF) under acidic conditions, several experiments with HMF as starting material were performed (Scheme 3). Without acid or iodide present, HMF was mainly hydrogenated in the presence of RhCl$_3$ and H$_2$ to form 2,5-dihydroxymethyltetrahydrofuran (**9**) as the principal product (reaction 1). Around 8 % DMTHF and a very small amount of tetrahydro-5-methylfuran-2-methanol (**5**) were also obtained. During this process, a significant amount of the added benzene was hydrogenated to cyclohexane. Upon the addition of either HI or NaI, DMTHF and **5** became the major products with a combined yield of ca. 75 % (reactions 2 and 3). Further, very little hydrogenation of benzene was observed. If acid was present in the form of HCl but no iodide, the yields of DMTHF and **5** were again greatly diminished (reaction 4) and a large amount of benzene was again hydrogenated to cyclohexane. The above experimental results clearly suggest that one critical role of the iodide ion is to suppress hydrogenation, especially of added benzene, and promote hydrogenolysis of CH$_2$–OH bonds. It has also been suggested previously that the iodide ion, by acting as a good nucleophile and leaving group, may promote the dehydration of glucose and fructose to HMF.[10] A detailed mechanistic study is required to fully delineate the role of the iodide ion.



Scheme 3. Conversion of 5-hydroxymethylfurfural (HMF). Reaction conditions: 1 mmol HMF; 0.05 mmol RhCl$_3$; 1.5 mmol HI, NaI, or HCl; 1.8 mL H$_2$O; 2 mL benzene; 300 psi H$_2$; 140 °C, 16 h.

Conclusions

We have demonstrated the feasibility of a one-step catalytic process to produce tetrahydrofuran derivatives for liquid fuels from a wide variety of carbohydrates and cellulosic biomass in good yields. The predominant product from hexose, DMTHF, is superior to ethanol and has many of the desirable properties that are currently found in typical petroleum-derived transportation fuels.

A one-step process generally requires less energy than processes that involve multiple steps, and the use of water as reaction medium is attractive. In addition, a variety of feedstocks, including raw lignocellulosic biomass such as corn stover, can be directly used without any chemical pretreatment. The optimized yields of tetrahydrofuran derivatives from cellulose (Table 5, entry 5) and corn stover (Table 6) appear to be the highest reported, and the purity of DMTHF from hexose and that of MTHF from pentose are relatively high. Finally, the catalyst system has been shown to be robust and can be recycled repeatedly without loss of activity.

Although the use of an expensive rhodium salt, the potentially corrosive acid, and dihydrogen clearly make the process uneconomical, we do show that in principle it is possible to "devise a simple, one-step or one-pot process that directly converts agricultural and municipal plant waste and other forms of raw biomass to valuable products."[12] A one-step, high-yield chemical process also compares favorably with typical bioconversions of lignocellulose that require three steps: lignocellulosic pretreatment, enzymatic hydrolysis of cellulose, and fermentation of sugars to make ethanol or other biobased chemicals.[26]

Experimental Section

Materials: Rhodium(III)chloride hydrate (Rh, 38.5–45.5 %) was purchased from Alfa Aesar. All carbohydrates were purchased either from Sigma–Aldrich or from Alfa Aesar. Cellulose was in powder form, with a particle diameter of around 20 μm. Corn stover samples were provided by the National Renewable Energy Laboratory (the compositional analysis of the sample is reported in the Supporting Information). The particle size of the corn stover used was ca. 0.5 mm. High-pressure hydrogen was obtained from GT&S, Inc. and used without further purification. Isotopically enriched chemicals, such as C_6D_6 and D_2O, were obtained from Cambridge Isotope Laboratories and used without further purification.

Typical Procedure for the Transformation of Carbohydrates to DMTHF: Carbohydrates (1 mmol, 6 wt % in water), HI (1.5 mmol, 57 wt % in water), $RhCl_3{\cdot}xH_2O$ (0.1 mmol), and organic solvent (4 mL) were added to a glass reaction vial in open air. The vial was then placed into a high-pressure stainless steel reactor, flushed with H_2, and charged with 300 psi of H_2. The reactor was then put in an oil bath and heated to 140 °C for 16 h. After the reaction was completed, the top organic layer was directly removed for analysis.

Typical Procedure for Transformation of Cellulose and Lignocellulose to DMTHF: Corn stover (0.18 g), $RhCl_3{\cdot}xH_2O$ (10 mg, 0.05 mmol), water (1.8 mL), HCl (70 μL, 0.8 mmol), NaI (300 mg, 2 mmol), and organic solvent (2 mL) were added to a glass reaction vial in open air. The vial then was put into a high-pressure stainless steel reactor, flushed with H_2, and charged with 300 psi of H_2. The reactor was then put in an oil bath and heated to 160 °C for 16 h. After the reaction was complete, the top organic layer was directly taken out for analysis. Procedures for the larger-scale reaction (10×) and isolation are in the Supporting Information.

Analysis Methods: The products were analyzed by ^1H NMR spectroscopy (Bruker Avance-360 spectrometer equipped with a quadnuclear probe operating at 360.13 MHz), GC (HP Hewlett Packard-5890 series II with an FID detector; 95 % dimethyl/5 % diphenylpolysiloxane column), and GC-MS (Waters GC-TOF with Agilent 6890 GC; 20 meter 150 um i.d., 0.15 um 95 % dimethyl/5 % diphenyl-polysiloxane film column; 70 eV electron ionization). The ^1H NMR spectra and the GC retention times of the products were also compared to authentic samples.

GC and GC-MS Analysis Methods: For GC analysis, the initial oven temperature was 40 °C; the temperature was then ramped at 3 °C min^{-1} until 100 °C was reached; after that, the temperature was ramped at 10 °C min^{-1} until 200 °C was reached, and held for 5 min. For GC-MS analysis, the initial oven temperature was 40 °C and held for 1 min; the program rate was 15 °C min^{-1} until 290 °C was reached, and held for 7 min. The total time elapsed was 25 min. The injector temperature was 290 °C with a split of 20:1. The helium flow rate was 0.5 mL min^{-1}. The temperature of the transfer line was 220 °C. The mass scan was 35–650 Da s^{-1}.

Quantification Methods: Products yields were determined from ^1H NMR spectra and GC analysis of the organic layer by using nitromethane as the internal standard. The yields reported were reproduced to within 5 %. Conversions were calculated based on ^1H NMR analysis of the aqueous layer, by using DMSO as the internal standard.

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