Biofuels

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Direct, High-Yield Conversion of Cellulose into Biofuel**

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These are days of great incentive in the field of bioenergy research. The stakes, of course, are immense—economic independence from politically unstable, petroleum-exporting countries, the remediation of greenhouse gas levels in the atmosphere and their potential effect on the climate, and mitigation of the economic consequences of our imminent arrival at the Peak Oil point, particularly in light of the pace of industrialization of emerging economic superpowers in Asia. It may be said that the final answer to the global energy issue will lie most credibly in ultraclean technologies based on hydrogen and solar energy.[1] However, few would deny a more immediate future to carbon-based fuels, in view of the prevailing automotive infrastructure based on the internal combustion engine, as well as the fact that the chemical industry will always require feedstocks for the production of organic materials and chemicals, regardless of what is being used for energy.[2]

The challenge to a new carbon-based fuel economy, as it emerges, is twofold: First, the carbon source must ultimately be atmospheric carbon dioxide, which is most practically harvested by the photosynthetic production of cellulose, hemicellulose, starch, and simple sugars, and second, these saccharides must be efficiently converted into molecules which are ambient temperature liquids of low volatility and high energy content. To some extent, the above challenge is currently being met by the production of ethanol from either starch-derived glucose or cane sugar, but this has largely been an issue of expediency, making use of mature technologies (agriculture and brewery/distillery) that were established long before energy became an issue, and the approach is now considered by many to be transitional.[3]

Since cellulose is by far the major form of photosynthetically fixed carbon, it can be argued that it should be the principal focus of any emerging carbon-fuel technology. The difficulty, from the point of view of ethanol production, is that fermentable sugars are not easily liberated from this material. The current model for cellulose utilization involves saccharification with immobilized enzymes, but despite recent advancements, this remains a slow and expensive process.

Our own interest in this area had less to do with the problems of cellulose hydrolysis than the poor carbon economy of glucose fermentation. Glucose is utilized by microorganisms according to the equation $C_6H_{12}O_6 \rightarrow 2\,C_2H_5OH + 2\,CO_2$. Even assuming quantitative efficiency both in the derivation of glucose from cellulose as well as the fermentation process, one third of the available carbon is expelled as carbon dioxide, 9.6 g of which is produced for every 10 g of ethanol. Effective approaches to biomass utilization which avoid fermentation altogether and exploit all of the available carbon present would thus be extremely valuable. Certainly, this point has not escaped the attention of researchers at the forefront of biomass conversion chemistry.[4] One promising direction this research has taken is towards "furanics", that is, high-energy, furan-based organic liquids. A high-profile contribution by Dumesic and co-workers in this area showed that fructose could be efficiently converted, via 5-hydroxymethyfurfural (HMF, **1**), into a range of substituted furan and tetrahydrofuran products.[5] If, however, this approach is to find broader application, it cannot rely on fructose as the source of HMF (**1**). Interestingly, a concurrent publication by Zhang and co-workers described the conversion of glucose into HMF (**1**) in record yield,[6] and taken together these two studies point towards a workable nonfermentive process for the conversion of glucose into biofuel. However, closer inspection of the latter of these papers shows that the expensive 1-ethyl-3-methylimidazolium chloride ionic liquid is used as the solvent which, along with chromium(II) catalyst, produces HMF in about 70 % yield, determined not by isolation but HPLC analysis. Along the same lines, Dumesic and co-workers have published a study in which HMF (**1**) is derived from glucose with 53 % selectivity at high conversion in 60 % aqueous DMSO in a biphasic reactor. While also promising, the separation of DMSO from HMF (**1**) remains an issue.[7]

Herein, we report that not only glucose, but cellulose itself, is converted into furanic products in isolated yields of greater than 80 % by conversion mainly into 5-(chloro methyl)furfural (CMF, **2**), a hydrophobic molecule which is easily sequestered into organic solvents in a two-phase reaction medium. The experimental setup we use to this purpose is a standard apparatus for continuous extraction of an aqueous solution with a solvent of greater density than water. Thus, microcrystalline cellulose was added to a stirred solution of lithium chloride (5 wt %) in concentrated hydrochloric acid to give a homogeneous mixture, which was introduced into a reaction chamber containing 1,2-dichloroethane. The solvent was heated to reflux and the aqueous slurry was kept at 65 °C with continuous mechanical stirring and extracted for 18 h. At this point, a further solution of LiCl in concentrated hydrochloric acid was added to the reaction chamber and extraction continued for another 12 h. The combined organic extracts were distilled to recover the solvent, and the residual liquid was chromatographed. The

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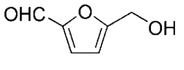
following products were isolated: 5-(chloromethyl)furfural (**2**, 71 %), 2-(2-hydroxyacetyl)furan (**3**, 8 %), 5-(hydroxymethyl) furfural (**1**, 5 %), and levulinic acid (**4**, 1 %). Filtration of the remaining aqueous layer gave a small quantity of fine, black, humic material (5 % by mass). The total, isolated yield of simple organics (**1**–**4**) is thus a remarkable 85 %. Applying the same reaction conditions to glucose gave **2** (71 %), **3** (7 %), **1** (8 %), **4** (3 %), and humic material (4 % by mass), for a total organic yield of 89 %. Finally, we were also interested in applying this method to sucrose, since it is currently the principal raw material used globally to produce bioethanol.[8] Here, we isolate **2** (76 %); **3** (6 %); **1** (4 %); **4** (5 %), and humic material (3 % by mass), for a total organic yield of 91 %.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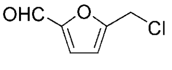
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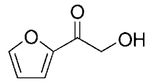
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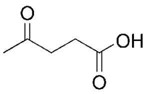
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Systematic variation of the time, temperature, and LiCl concentration of the reaction have shown that these parameters are very nearly optimal for glucose, sucrose, and cellulose using the present experimental setup. The quantity of HCl/LiCl solution and dichloroethane solvent used was a matter of convenient handling and has not been optimized.[9] The nearly identical results obtained for cellulose and glucose suggest that the rate-limiting component of the process is not the hydrolysis of cellulose, but the dehydration of glucose or the dropwise extraction of the furan products. A more aggressive extraction protocol would almost certainly reduce the reaction times, and we will address the optimization of this variable in a future report.

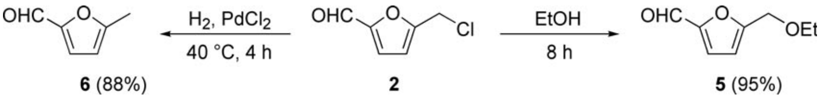
While CMF (**2**) is itself not a biofuel candidate, it is converted into ethoxymethylfurfural (EMF, **5**) in nearly quantitative yield by stirring it in ethanol solution at room temperature (Scheme 1). Interestingly, EMF (**5**), a liquid with a boiling point of 235 °C, is already considered to be a promising alternative fuel, the energy density of which is reported to be 8.7 kWh$\,L^{-1}$, substantially higher than that of ethanol (6.1 kWh$\,L^{-1}$), and comparable to that of standard gasoline (8.8 kWh$\,L^{-1}$) and diesel fuel (9.7 kWh$\,L^{-1}$).[10] EMF (**5**) has been tested in blends with diesel fuel by Avantium Technologies, a spin-off of Royal Dutch Shell, who noted that "the test yielded positive results for all blends tested. The engine ran smoothly for several hours. Exhaust analysis uncovered a significant reduction of soot."[11]

Alternatively, CMF (**2**) could be hydrogenated in 88 % yield using $PdCl_2$ under mild conditions to give 5-methylfurfural (MF, **6**, b.p. 187 °C), thus avoiding the need for ethanol in the derivation of a useable biofuel from **2** (Scheme 1).[12] Hydrogenation of CMF (**2**) using a Pd/C catalyst is reported to give 2,5-dimethylfuran, b.p. 94 °C, in high yield,[13] while complete reduction would give 2,5-dimethyltetrahydrofuran, b.p. 92 °C. Both of these latter molecules are key products in the dehydration/reduction of HMF (**5**) reported by Dumesic and co-workers,[5] and are reduced relative to **2** by three and five equivalents of H_2, respectively. The facile hydrogenation of such molecules makes them credible media for "hydrogen storage", considering that the difference of five moles of H_2 between **2** and 2,5-dimethyl-tetrahydrofuran represent 10 % of the mass of the latter. While a chromatographic separation is important to establish the actual chemical yields of the products in this study, treatment of the crude extracts containing **1**–**4** with ethanol or H_2/catalyst and direct isolation **5** and **6** by distillation is equally feasible.[14]

Since there have been general concerns about the potential health hazards of oxygenated fuels, it is worth briefly commenting here on the toxicity of **5** and **6**. A material safety data sheet (MSDS) for EMF (**5**) has not been published, but **5** would most likely be hydrolyzed in vivo into HMF (**1**) and ethanol. HMF (**5**) is a flavor component in many foods,[15] and is even considered a potential anti-tumor agent.[16] It is listed in its MSDS as a low health hazard (Category 1) and a mild irritant. An MSDS has been published for MF (**6**), where it too is listed as a Category 1 hazard. Furthermore, it is important to note that the vapor pressures of **5** and **6** are far lower than that of toxic fuel oxygenates such as methyl *tert*-butyl ether, and so the principal means of exposure for most people (during automobile refueling) would be less of a concern in this case. On the positive side of this issue, in a future biofuel-100-compatible vehicle market, the use of oxygenated fuels which have no (known) potential for abuse as inebriants may actually prove an advantage.

Although reports of CMF (**2**) are relatively uncommon in the chemical literature, it was described as early as 1901 as a product from the action of dry hydrogen chloride on cellulose.[17] While the conversion was low (12 %), a related study in which anhydrous HBr was employed showed that the bromo analogue of **2** could be produced from cellulose in up to 48 % yield, although glucose itself underwent the reaction in only 11 % yield.[18] Finally, a number of other reports address the preparation of CMF (**2**) from fructose,[19] which is consistent with the related, facile conversion of the latter into HMF (**5**).[20] Nowhere in the literature is glucose described giving CMF (**2**) in good yield.

In conclusion, glucose, sucrose, and cellulose are readily converted into 5-(chloromethyl)furfural (**2**), a stable, hydrophobic organic liquid. Small quantities of related furans HMF (**1**) and 2-(2-hydroxyacetyl)furan (**3**)[21] as well as levulinic acid (**4**)[22] are also isolated, bringing the total yield of simple organic compounds to 85–91 %. CMF (**2**) is easily converted into the known biofuel EMF (**5**) or catalytically hydrogenated to MF (**6**). The method, as reported here, 1) constitutes the highest



Scheme 1. Conversion of CMF (**2**) into EMF (**5**) and MF (**6**).

yielding conversion of cellulose into simple, hydrophobic organic molecules yet described; 2) significantly exceeds the usable carbon yield of glucose/sucrose fermentation but, unlike fermentation, *is able to utilize cellulose directly*; and 3) provides a solution to the long-standing glucose to HMF (**1**) conversion problem,[6,7] given that CMF (**2**) can be easily hydrolyzed to HMF (**1**).[20b] While future reports will address further optimization, scaleup, and applications of the method to raw biomass, these preliminary results suggest that this simple, efficient approach to cellulose deconstruction has the potential, at the very least, to complement fermentation as a means to produce biomass-derived automotive fuels, and to establish furanics both as a renewable energy source and industrial chemical feedstock of the future.

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