

High-Yield Chemical Conversion of Biomass into Biofuels and Value-Added Products

Mark Mascal* and Edward B. Nikitin

Department of Chemistry, University of California Davis, 1 Shields Avenue, Davis, CA, USA
mascal@chem.ucdavis.edu

ABSTRACT

We have developed a new method to efficiently convert waste biomass (agricultural, municipal, forestry) into biofuels and value-added products. The process is completely chemical in nature, inexpensive, and produces no waste stream. The derived products are non-toxic, biodegradable substitutes for petroleum, both in motor fuels and as renewable chemical intermediates. The technology involves the chemical digestion of the carbohydrate content of biomass (sugars, starch, cellulose, hemicellulose) in a proprietary biphasic reactor under mild conditions (80 °C, 2-3 h) to give 5-(chloromethyl)furfural (CMF) as the main product in isolated yields as high as 90%. To our knowledge, no other method of biomass deconstruction gives such complete conversion of carbohydrates into a simple organic molecule. We present CMF here as an emerging renewable platform chemical, providing access to a versatile portfolio of derived products.

Keywords: biofuels, biomass conversion, cellulose, furans, levulinates

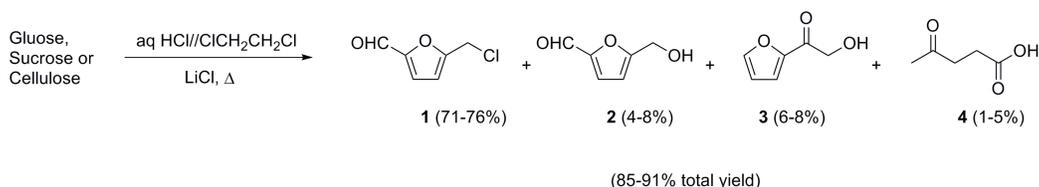
1 INTRODUCTION

1.1 Background Chemistry

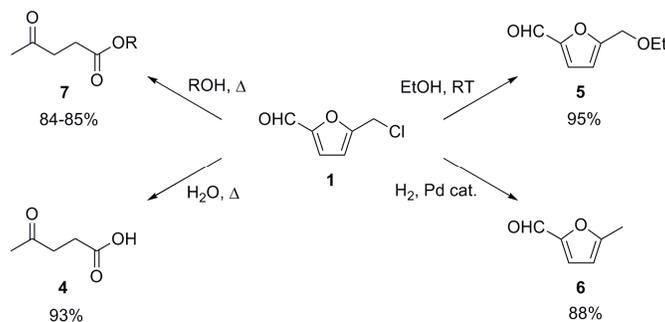
In 2008, we reported that glucose, sucrose, and microcrystalline cellulose could be converted into a mixture of 5-(chloromethyl)furfural (CMF) **1**, 5-(hydroxymethyl)furfural (HMF) **2**, 2-(2-hydroxyacetyl)furan **3**, and levulinic acid **4** in combined yields of up to 90% by simple reaction with an aqueous HCl-LiCl solution (Scheme 1).^[1] The process involved heating a mixture of the substrate with the HCl-LiCl reagent at 65 °C in a biphasic reactor with continuous circulation of a solvent. The resulting "crude oil" was a mixture of compounds **1-4**. CMF **1** was by far the major component, and is a versatile chemical intermediate from the perspective both of biofuels and value-added organic products. For example, **1** can be converted into 5-(ethoxymethyl)furfural (EMF) **5** by simple mixing with ethanol (Scheme 2). EMF, a liquid with boiling point 235 °C, is already being commercially developed as a promising diesel fuel blending agent.^[2] We have measured the energy density of **5** to be 30.3 MJ L⁻¹, similar to that of gasoline (31.2 MJ L⁻¹) and superior to that

of ethanol (23.5 MJ L⁻¹). Alternatively, hydrogenolysis of the halogen in **1** gives 5-methylfurfural (MF) **6**, bp 187 °C, which we consider to be a particularly attractive biofuel candidate, since only 2 g of H₂ are required for the synthesis of 110 g of **6**, as opposed to 46 g of ethanol in the synthesis of 154 g of **5**. Reaction of CMF **1** with alcohols at higher temperatures leads directly to levulinic esters **7**.^[3] We have prepared both ethyl and butyl levulinate (R=Et and Bu, resp.) in this manner. Ethyl levulinate is a non-toxic γ -keto pentanoate ester with boiling point 206 °C and flash point 91 °C. It has good lubricity and has been tested in blends with petroleum diesel up to 10% with no change in cetane number.^[4] Its shorter chain length suggests the potential to favorably impact the properties of biodiesel in terms of its cold performance issues (cloud point, pour point, viscosity).^[5] Finally, simple hydrolysis of **1** gives levulinic acid (LA) **4** in high yield. LA has the distinction of appearing on the list of Top Value-Added Chemicals From Biomass published by the US Department of Energy's National Renewable Energy Laboratory (NREL). This list of twelve, mainly sugar-derived products was assembled in order to identify major opportunities for "the production of value-added chemicals from biomass that would economically and technically support the production of fuels and power in an integrated biorefinery, and identify the common challenges and barriers of associated production technologies."^[6] In its candidate summary biography, LA is referred to as "one of the more recognized building blocks available from carbohydrates," the derivatives of which "address a number of large volume chemical markets." These derivatives include levulinate esters and 2-methyltetrahydrofuran (fuel additives), δ -aminolevulinic acid (herbicide), and β -acetylacrylic acid, diphenolic acid and 1,4-pentanediol (polymer building blocks).

It is important to note that the stoichiometry of the overall reactions to make these products leaves *nothing* that cannot be recycled in this process. For every molar equivalent of cellulose, one molecule of water is consumed to give glucose. In the ensuing formation of CMF **1**, one molecule of HCl is used and four molecules of water are produced. Then, in the production of **4-7**, one molecule of alcohol, water, or hydrogen is consumed and the molecule of HCl is returned. The method also requires the use of an extraction solvent; in the reaction in Scheme 1 the solvent was ethylene chloride. In principle, any hydrophobic solvent could be used with appropriate modifications to the



Scheme 1: Biomass conversion process.



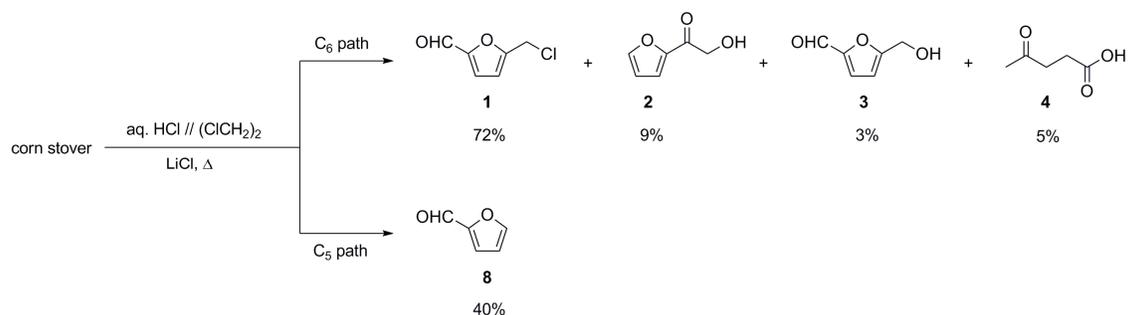
Scheme 2: Derivatives of CMF. R = Et or Bu.

reactor, and in any case, the solvent is employed in a closed extraction loop and is thus completely recycled.

1.2 Processing of Raw Biomass

The real test of the above method was whether it could also operate on cellulosic waste materials (*e.g.* agricultural, municipal, forestry). We thus subjected cotton, straw, corn stover, newsprint, and wood chips to the same conditions as outlined above for pure cellulose.^[7] In each case, we obtained a similar mixture of compounds **1-4**. In order to determine the chemical yield, we acquired an analyzed sample of corn stover from NREL. Based on the carbohydrate content of the corn stover, the isolated yields of products turned out to be **1**, 72%; **2**, 3%, **3**, 9% and **4**, 5%, for a total of 89%, which was entirely consistent with that of pure cellulose itself. This means that the conversion process was unaffected by the presence of the other components in raw biomass. Lignin, for example, survives the reaction essentially unchanged and can simply be filtered off. Any protein which is present is hydrolyzed and turns up in the aqueous phase as a mixture of amino acid salts.

Interestingly, we also isolated furfural **8** from the reaction mixture, which was clearly the result of the same cyclization-dehydration processes operating on the hemicellulose fractions of the feedstocks (Scheme 3). Hemicellulose, which consists mainly of C₅ sugars, is the second most-abundant organic material in nature, typically representing 25–35% of lignocellulose by mass. In mainstream ethanol production, this vast resource goes unutilized, because native yeasts do not generally ferment C₅ sugars. The yield of **8** (40%) is lower than the combined yield of **1-4**, but is consistent with reported yields of furfural from biomass in commercial processes, which are typically around 50% of the theoretical, so it appears that modest yields are intrinsic to the conversion of C₅ sugars into **8**. The key point here is that we have accomplished *the total carbohydrate utilization of biomass*, where the cellulose fraction produces mainly **1**, which may be processed into derivatives like **4-7**, while the hemicellulose fraction gives furfural **8**. Furfural is a chemical commodity which is produced globally as a feedstock for resin manufacture and as a precursor to a range of specialty chemicals, including fuel additives.^[8]



Scheme 3: Raw biomass conversion.

Another key feature of this process is that only simple mechanical pretreatment of the feedstock is required. In the case of cotton or newspaper, the substrate was shredded into small pieces ca. 0.5 cm on a side. For straw, corn stover, and wood, the material was milled to a coarse powder. This is significant when one considers the high expense involved in the pretreatment of biomass for enzymatic digestion, which usually involves a denaturing technique such as steam, ammonia, or supercritical fluid explosion.

2 CURRENT STATE OF THE ART

2.1 Process Upgrades

In recent work, we have described some dramatic improvements to the above process, including the following:

a) *A substantial acceleration of the reaction rate.* Whereas the reaction in Scheme 1 used to take up to 30 hours to reach full yield, it is now complete within 2-3 hours. This was achieved by running the reaction at a higher temperature (80 °C) in a closed vessel.

b) *A >20-fold reduction in extraction solvent usage.* We originally described a continuous extraction method which required the circulation of several liters of solvent through the reaction mixture. This has now been replaced with a serial extraction protocol requiring much less solvent.

c) *Elimination of the use of the LiCl catalyst.* The method as originally described employed a lithium salt as a cellulose swelling agent. The improved reactor design and efficiency have eliminated the need for this.

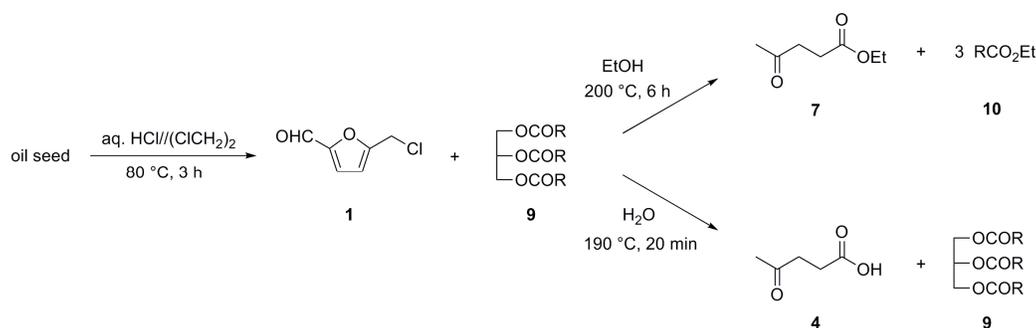
d) *Increase in substrate loading in the reactor to 10% w/v.* The reactor loading in our initial work was about 1%. The improved reaction efficiency allowed for more practical substrate loadings of up to 10%.

e) *Improvement of the yield of CMF 1 from sugars, cellulose, and corn stover.* In the upgraded process, there are only two products, CMF 1 and LA 4. Minor products 2 and 3 from Scheme 1 are no longer observed. Depending on loading, CMF yields are between 70-90%, and LA yields are 5-9%. The yield of 1+4 from cellulose is 84-89%. Record yields are attained using sucrose as the substrate, which can be as high as 95% of the theoretical.

6) *Extension of the method to chitin as a feedstock.* Chitin, a 1,4- β -linked *N*-acetyl-2-amino-2-deoxy-D-glucan, is best known as the structural component of the exoskeletons of insects and crustaceans, and is second only to lignocellulose in natural abundance. It is a high tonnage waste product of the seafood industry. Chitin is exceptionally insoluble and resistant to hydrolysis, and yet it too can be made to give a mixture of 1+4 at a higher temperature (150 °C) and pressure (ca. 200 psi).^[9]

2.2 Application to Biodiesel Production

The above technology has also been integrated with the extraction of triglycerides from oil crops to produce a hybrid lipidic-cellulosic biodiesel.^[10] *Using this method, we are able to increase the yield of fuel from biodiesel feedstocks by as much as 25%.* The basic concept is that oil seeds (e.g. camelina, canola, jatropha, safflower, soybeans) contain not only oils but also significant carbohydrate profiles, in the form of starch, cellulose ("fiber"), hemicellulose, and free sugars. When processed under the conditions described above, a mixture of CMF 1 and the triglyceride 9 is obtained. No hydrolysis of the triglyceride is observed, since the oil is quickly sequestered into the organic phase of the reactor. This mixture can be treated in either of two ways: Heating with ethanol directly gives a cocktail of biodiesel 10 and ethyl levulinate 7 in high yield. As mentioned previously, fatty acid/levulinate ester blends are predicted to have better cold-performance properties than pure biodiesel. To illustrate, the pour point (ASTM D97) of B100 is -3 °C, whereas that of 7 is -50 °C. When we use safflower as the feedstock, enough ethyl levulinate 7 is produced by this method to increase the amount of fuel by 25% over simple transesterification of the oil itself. Alternatively, heating 1+9 in water gives a mixture of the unchanged oil 9 and levulinic acid 4 (Scheme 4), which offers maximum versatility to use the raw products 4 and 9 to whatever purpose is most appropriate. Finally, the *entire plant*, including stalks, leaves, and shells can also be harvested and utilized for biodiesel production, not just the seeds, in which case the main component of the extract becomes CMF 1, since there is now more carbohydrate than lipid present. Preliminary results using high oil-content algae have also been promising.



Scheme 4: Oil seed processing. R = fatty acid alkyl chain.

3 CONCLUSION

To summarize, the technological advantages of the above described process are the following:

In terms of innovation, this approach stands alone in the area of biomass conversion research. To date, no other reported technology centers on CMF **1** as a biomass-derived platform chemical for biofuels and value-added materials.

The yield is extraordinary. We know of no other biomass conversion process, whether operating from simple sugars, cellulose, or raw biomass, that gives such high isolated yields of simple organic products.

Mixed-source lignocellulosic feedstock can be directly utilized with minimal pretreatment. Sources may include forestry, agricultural or municipal wastes. Only mechanical reduction to a reasonable particle size is required. Since the process is aqueous, even drying of the substrate is not necessary. The use of the unconventional feedstock chitin may present an opportunity for the gainful remediation of solid waste from the seafood processing industry.

The reagents are inexpensive and the process operates under mild conditions. No complex catalysts, enzymes, microorganisms, or extremes in temperature are involved. Everything is recycled, there is no waste stream, and the only non-organic product is water.

The derived products are drop-in, environmentally friendly fuel candidates. Reaction of CMF **1** with alcohols or H₂ produces EMF **5**, MF **6**, or levulinate esters **7** which are compatible with the existing automotive infrastructure. These are hydrophobic, non-volatile, non-malodorous, low-toxicity, non-corrosive, sulfur-free, biodegradable, high energy liquids. Reaction of CMF with water gives levulinic acid **4**, a key renewable, value-added organic chemical intermediate.

The method is entirely compatible with the extraction of triglycerides from oil crops. The merger of lipid- and cellulose-based biomass conversion technologies has the potential to define a new biodiesel industry.

In conclusion, we have described a simple, efficient process for the conversion of plant biomass into 5-(chloromethyl)furfural **1**, the derivatives of which may be applied to a variety of purposes in the materials and fuel industries that would otherwise involve the expenditure of petroleum. We suggest that CMF **1** may emerge as a central carbohydrate-derived organic platform chemical, and biphasic acid/solvent lignocellulose digesters as the method of choice for exploiting waste biomass.

4 REFERENCES

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