

Conversion of sugars into hydrocarbons for blending into jet and diesel fuels: general considerations

David K. Johnson, david.johnson@nrel.gov

Biosciences Center, National Renewable Energy Laboratory (NREL), Golden, CO 80401

Abstract

To transform biomass into components compatible with hydrocarbon fuels it is clear there are two main transformations that need to occur, deoxygenation and carbon chain extension. Deoxygenation is necessary to increase energy content and to compatibilize the components with existing petroleum-derived fuels. Chain extension is needed to convert intermediates derived from biomass, such as five and six carbon sugars, into components with the correct boiling range for blending with specific fuels. Through these transformations it becomes possible to produce drop-in fuels that are transparent to the consumer, have unlimited blendability, and can utilize existing infrastructure for storage and transportation.

The development of transformation routes that efficiently convert biomass-derived intermediates into products that are compatible with the existing fuel infrastructure, which fit within the specifications for gasoline, jet and diesel fuels, is currently an area of intense research interest. The potential routes for decreasing the oxygen content of biomass intermediates include decarboxylation, dehydration, and hydrodeoxygenation. Rejection of oxygen as carbon dioxide, decarboxylation, results in significant carbon and mass loss from sugars, while rejection of oxygen as water, dehydration, leads to unsaturated products and undesirable tars. Hydrodeoxygenation, using hydrogen to remove oxygen as water, produces saturated products and retains carbon, however, uses expensive hydrogen, catalysts and often severe conditions. This presentation will discuss the difficulties in converting sugars to hydrocarbons and compare the different routes using practical examples to highlight the impact of choosing one route over another.

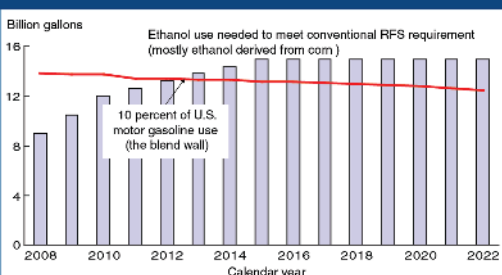
Why Change to Drop-in Advanced Biofuels

- E10 blend wall
- 10% Ethanol blend insufficient to meet RFS legislation
- 15% Ethanol blend needed
- E85 Unpopular
- Avoid complex consumer choice
- Additional pumps expensive
- Cost of transporting alternatives
- Drop-in hydrocarbon fuels
- Transparent to the consumer
- Unlimited blendability
- Advanced biofuels can include renewable jet and diesel fuels



E10 blend wall forecast to constrain compliance with conventional Renewable Fuel Standard (RFS)

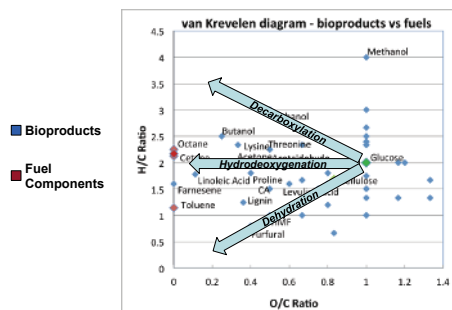
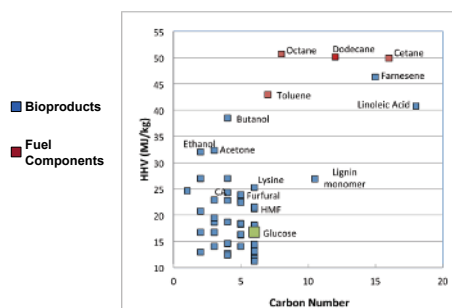
E10 blend wall and ethanol use needed to comply with conventional RFS



RFS = Renewable Fuel Standard. E10 = 10-percent ethanol/gasoline blend. Sources: USDA, Economic Research Service calculations derived from U.S. Department of Energy, Energy Information Administration, Annual Energy Outlook, 2013 and the Energy Independence and Security Act of 2007.

How Can We Make Hydrocarbons from Biomass-derived Components

- Increase energy content - Decrease oxygen content
- Increase carbon chain length - especially for jet and diesel fuels



Top Value Added Chemicals from Biomass Volume I - Results of Screening for Potential Candidates from Sugars and Synthesis Gas (2004). Top 30+ chemicals

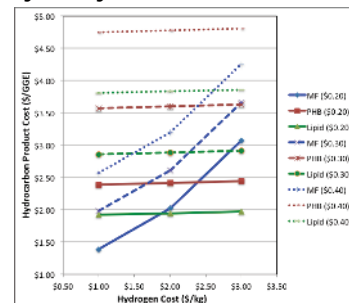
- Decarboxylation - significant mass and C loss
- Dehydration - unsaturated products and tars produced
- Hydrodeoxygenation (HDO) - gives saturated products, conserves mass, but uses expensive H₂/catalysts, severe conditions

- There are reasonable high yield pathways for producing hydrocarbons from sugars using decarboxylation and hydrodeoxygenation that would give hydrocarbons that fit within the jet and diesel fuel ranges
- Depolymerization and decarboxylation of PHB produces propene that can be converted into higher hydrocarbons
- Xylose can be dehydrated into furfural and then hydrogenated to methyl furan which will selectively condense with aldehydes to make C12-C15 intermediates. HDO of methyl furan condensation products gives hydrocarbons which could be superior jet and diesel fuel blending components.
- Hydrogenating oxygenates to produce fuels equivalent to storing H₂ at many 1000s psi.
- It is too early to say which pathway is likely to be the best. This will only come after detailed TEA and energy balance analyses can be conducted.
- Hydrogen supply and cost is likely to be a challenge to the cost and sustainability of advanced biofuel processes
- Sugar costs need to be further decreased to allow us to meet DOE targets

Which Pathway to Hydrocarbons is Best

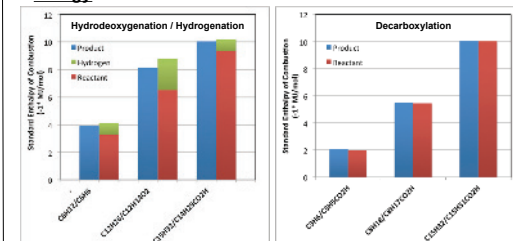
Cost

MF = Methyl furan pathway
PHB = Polyhydroxybutyrate pathway
Lipid = Lipid pathway
(Sugar cost \$/kg)



- NREL Biochemical Platform Analysis project performs detailed TEA
- Many factors contribute to final cost: yields, process conditions, capital equipment, catalyst longevity
- Simple comparison based on theoretical yield and H₂ consumption
- Methyl furan (MF) pathway with HDO favored by low cost H₂
- PHB pathway less favored because too much C lost in decarboxylation
- Lipid pathway favored because not all O rejected as CO₂

Energy



- How much of the energy in the reactants is retained in the products
- Many factors contribute to energy balance - yields, process conditions/process integration
- Simple comparison based on exo/endo-thermicity of the reactions
- Decarboxylation reactions tend to be very slightly endothermic
- Hydrogenations and HDO reactions tend to be strongly exothermic
- Heat content of hydrocarbons relative to starting materials (incl. H₂)
decarboxylation ~1% higher; hydrogenation/HDO 1-7% lower