Webinar: “Upgrading Renewable and Sustainable Carbohydrates For the Production of High Energy Density Fuels”

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Biomass Program Overview:
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Hydrocarbon Presentation: Pete Silks and John Gordon, LANL
Biomass Program Vision, Mission, and Strategic Goal

**Vision**

A viable, sustainable domestic biomass industry that:
- Produces renewable biofuels, bioproducts, and biopower
- Enhances U.S. energy security
- Reduces our dependence on oil
- Provides environmental benefits, including reduced greenhouse gas (GHG) emissions
- Creates economic opportunities across the nation.

**Mission**

Develop and transform our renewable biomass resources into commercially viable, high-performance biofuels, bioproducts, and biopower through targeted research, development, demonstration, and deployment (RDD&D) supported through public and private partnerships.

**Strategic Goal**

Develop commercially viable biomass technologies to enable the production of biofuels nationwide and reduce dependence on foreign oil through the creation of a new domestic bioenergy industry, thus supporting the EISA goal of 36 billion gallons per year of renewable transportation fuels by 2022, and increase biopower’s contribution to national renewable energy goals by increasing biopower generating capacity.
Expanding Scope

The Biomass Program forms cost-share partnerships with key stakeholders to develop, demonstrate, and deploy technologies for advanced biofuels, bioproducts, and biopower from lignocellulosic and algal biomass.
The need to reduce dependence on foreign oil and lower GHG emissions has renewed the urgency for developing sustainable biofuels, bioproducts, and biopower.

The transportation sector accounts for about two-thirds of U.S. oil consumption and contributes to one-third of the nation’s GHG emissions.

Near-term, biomass is the only renewable resource that can supplement petroleum-based liquid transportation fuels, while reducing GHG emissions.

Biomass includes agricultural residues, forest resources, perennial grasses, woody energy crops, wastes (municipal solid waste, urban wood waste, and food waste), and algae, as well as other sources. It is unique among renewable energy resources in that it can be converted to fuels and chemicals—in addition to power.
Biomass Program Webinar Series

• Started in May 2010 to highlight “hot topics” in Biomass.

Find past webinars, as well as slides from this webinar, on the Biomass Program website: biomass.energy.gov/webinars.html.
Questions?

Please type in your questions as you have them during the webinar.

All slides from this presentation can be found on the Biomass website next week:
www.eere.energy.gov/biomass/webinars.html

Email John Gordon and Pete Silks with additional questions regarding the topic: jgordon@lanl.gov and pete-silks@lanl.gov

For questions regarding the Biomass Program, please email the Program: eere_biomass@ee.doe.gov
Upgrading of Carbohydrates into High Energy Density Fuels

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LANL direct catalytic chain extension, (e.g. ketone plus a furan aldehyde) then HDO to alkane.

NOTE: Algal Starch has several advantages

* Companies such as Incitor are accessing furanics and levulinates from raw non-food based biomass with about ~10x decrease in current costs.

* HDO = hydrodeoxygenation (oxygen/hydrogen exchange on carbon chain).
Integrate Expertise at LANL in Order to (Catalytically) Convert Cellulosically Derived Feedstocks into High Energy Density Fuels

**Development of effective biomass conversion technologies that Integrates with existing fuel production and distribution infrastructure:**

*Enable shift away from our dependence on foreign petroleum imports.*

*Funding from LANL LDRD & CRADA*

![Diagram showing glucose and arabinose conversion to cellulose-derived polyols through Aldol Organocatalysis and Hydrodeoxygenation Catalysis, leading to reactor design and high energy density C₈-C₁₅ Fuels.](image-url)
The General Paradigm...

Low oxygen content
Underfunctionalization problem

- Crude Oil
- Gas

- Amination
- Oxidation
- Hydration

- Hydroformylation
- Hydrocyanation
- Dehydrogenation

- Petrochemicals
  - Monomers/Polymers
  - Fine Chemicals

- Dehydration
- Hydrogenation
- Hydrogenolysis

> 100 years R&D

High oxygen content
Overfunctionalization problem

- Biomass:
  - Sugars/Sugar polyols

- Dehydration
- Hydrogenation
- Hydrogenolysis

- Biofermentation

relatively little R&D

Consumer products

M. Schlaf, *Dalton. Trans.* 2006, 4645
The bulk of typical gasoline consists of hydrocarbons with between 4 and 12 carbon atoms per molecule.

Chemical structure of iso-octane used as the standard for fuel octane ratings

High Energy Density Fuels – require longer hydrocarbon chains than those provided to us by C_5 and C_6 sugars; i.e. C-C chain extension is required

Petroleum-derived diesel is composed of about 75% saturated hydrocarbons. The average chemical formula for common diesel fuel is C_{12}H_{23}, ranging from approx. C_{10}H_{20} to C_{15}H_{28}.

Kerosene-type jet fuel (including JP 8 and 76) has a carbon number distribution between C_8 and C_{18}.
Addressing Chain Extension

An easy initial route was to propose to do this using derivatives of sugars. Furans like HMF are obtained in 60% yield from corn stover (agricultural by-product) and have been a target for conversion to fuels.

Ideal for proposal - the aldehyde is perfectly set up for carbon chain extension since it is non-enolizable (fewer side reactions...)

Hydroxymethylfurfural (HMF)
IUPAC: 5-(hydroxymethyl)-2-furaldehyde

Others have also targeted the use of furans for fuel production:

• *Dumesic.*

• *Virent uses the conversion of furans to hydrocarbons.*

• *World wide production of these furans has ramped up. Exponential increase of publications showing new ways to economically create these furans from sugars.*
Synopsis of Initial Approach

6-carbon sugar

organocatalyzed aldol

9-carbon polyol

organocatalyzed aldol

$C_{12}$ hydrocarbon
diesel-like

dehydrations/hydrogenations

12-carbon polyol
Background: Feasibility Of Chain Extension Reactions Using Bioderived Synthons??

Various aldol coupled products subjected to aqueous phase dehydration/hydrogenation using e.g. Pt/SiO₂/Al₂O₃
Typical temps 500-600K; typical H₂ pressure ~55 bar
Requires organic solvent and water

Our Starting Point for C-C Coupling: Take Lesson from Nature: Aldolase Mimics...

Initial Attempts:

- Aldolase enzymes contain amino acid residues that can catalyze the (reversible) formation of C-C bonds in vivo

- Use of proline in DMSO at RT failed with [1,2,3-13C₃]DHADA and benzaldehyde.......

- Use of proline in DMSO at elevated temperatures failed....

- Use of proline in water failed...
Make it work - Take a Lesson From Aldolases..?

Single coupling between acetone and HMF

Can also get double coupling (excess HMF)

Piperidine as Catalyst for C<sub>9</sub> and C<sub>15</sub> Fragment Syntheses (100 g quantities)…!!!

HMF + Acetone; in water, at ambient temperature, overnight
Piperidine as Catalyst for $C_9$ and $C_{15}$ Fragment Syntheses: Water Orders Transition State (LANL Capabilities Leveraged)

Theoretical Division

Center for Nonlinear Studies

Optimized the Aldol Reaction for Carbon Chain Extensions!!!!

I. Uses the cheapest biomass material known to date (Furfural is ~80 cents/lb)
II. > 99% Conversion, 95% Isolated Yield
III. No Solvent (Neat Reaction)
IV. Room to Below Room Temperature
V. Organocatalyst: Pyrrolidinium acetate.
VI. Simple Work up (Just add water)
VII. Works on Multiple Systems

“Compounds and Methods For the Production of Long Chain Hydrocarbons From Biological Sources”, US and PCT Patent Applications. NOTE: both process and composition of matter covered.
Converting Aldol Products into Alkanes

Steps required:

- Ring opening of furans
- Hydrogenation of olefins
- Hydrodeoxyxygenation of ketones
Interrogation of Aldol Derived C₉ Precursor as Model System

Key first step – removal of exocyclic C=C group:

\[
\begin{align*}
R' & \quad \text{MeOH} & \quad R
\end{align*}
\]

50 – 60 % isolated yield

\[
\begin{align*}
R & \quad \text{MeOH} & \quad R
\end{align*}
\]

R = H, alkyl
R' = OH, H

64 – 93 % isolated yield

\[
\begin{align*}
R' & \quad \text{MeOH} & \quad R
\end{align*}
\]

R = H, alkyl, aryl, -CO₂C₂H₅
R' = -OC₂H₅, -NH₃, -CH₃, -CH=CHC₆H₅

Ram & Spicer, *Synthetic Communications*, 1992, 22(18), 2683-2690

~ 85 % isolated yield
Moved to Pressurized Systems with H₂

Following H-transfer reagents, move to H₂ pressure to simplify work-up:

In THF fully saturated ring can be prepared:

However, switching solvent. Clean reaction – simple work-up
What About Reaction Stoichiometries (H₂ uptakes) and Product Yields?

Reservoirs allow H₂ uptake measurement at constant pressure,

Mass flow meter is the black object

ADC interface is the white box

The blue object is an independent digital pressure gauge

Max. design pressure = 1800 psi

Max. operating pressure = 1500 psi

Max. temp. = 250 °C

Head space and solution samples removed after hydrogenation for analysis by GC-MS
Further Refinement – Multi-Step (w/U.Guelph)

0.1 wt % Pd (using 5% Pd/C)
50/50 (w/w) HOAc/H₂O

65 °C, 2-3 h

Up to 98 % isolated yield
Then isolated Triketone to Nonane

B

1 wt% Pd (5% Pd/C)  
50 wt% La(OTf)_3  
Glacial HOAc  
500 psi H_2 (g), 200 °C  
16 h

C

One Product (GC-MS):  
6 eq. H_2 taken up  
100% conversion  

~90% conversion  
from aldol product to alkane,  
no triketone remaining  

Possibly coking for the remaining 10%,  
Minimal CO_2 in headspace
C\textsubscript{9} Reaction Pathway

- All intermediates can be isolated and reactivity shown
- Initial hydrogenation is key
- Ring opening vs. full hydrogenation
- Once the ring is hydrogenated conversion to alkane does not proceed under our conditions
- High H\textsubscript{2} pressure favors ring hydrogenation
Chemistry Generally Applicable to Other Chain Lengths

Method is general to generate other polyketones, which can then be subjected to HDO to make array of alkanes UNDER MILD CONDITIONS....


*Catalysis Science and Technology 2012, Hot Article* (asked to submit cover graphics)
What About Alkanes Directly from Sugars?

Undressing Algal Starch: Two Step Process to Hydrocarbons

Starch, soluble + \( \text{CeCl}_3 \cdot 7\text{H}_2\text{O} \) (10 mol%) \( \text{HCl} \) (10 mol%) \( \text{H}_2\text{O} \), reflux \( \sim 3 \text{ days} \)

1.97 g ca. 11 mmol of glucose
1.50 mL 14.61 mmol

\( 1 \) (major) 14.61 mmol of glucose

>99% conversion by TLC (no baseline spot)
1.86 g (crude, after extraction)
ca. 75% recovered.
Undressing Algal Starch: Two Step Process to Hydrocarbons

Use of an inexpensive Iron catalyst. Attacking the sourcing costs.

Glucose

Pretreatment then

Cat \( \text{Fe(OTf)}_3 \), water, heat

R = iPr, Et

Three cycles
74%, 90%, 95%

Demonstrates catalyst activity
Is inert to reuse.

Algal or Potato soluble starch

Pretreatment then

Cat \( \text{Fe(OTf)}_3 \), water, heat

R = iPr, Et

~74%

Demonstrates similar activity using starch compared to glucose.

Completed reaction upon Cooling. Biphasic: Easy Separation and offers simple flow through reactor set-ups.
HDO on GG Product to Give Branched Hydrocarbons

Other potential oligosaccharide sources include cellulose, hemicellulose, cotton, and chitin.
Note: Starch from Algae is Lignin free
Leveraging LANL Stable Isotope Resource Capabilities: Synthesis of Labeled Precursors Readily Allows the Interrogation of Reaction Pathways and Easy Optimization of Conditions

Organocatalyzed reaction of $[1,2,3^{-13}\text{C}_3]\text{DHA} + \text{HMF}$

\[ \begin{array}{c}
\text{Organocatalyst} \\
\text{soluble starch} \\
\text{Catalyst} \\
\end{array} \]

Use mass spectrometry to Quickly assess reaction status

$^{13}\text{C}$ labeled HMF from Glucose using Lanthanide Catalyst ($\text{Yb(OTf)}_3$, 10%, in water) i.e. integrates dehydration chemistry in water with isotope labeling
Russets to Alkanes...???????
Conclusions and Future Work

Conclusions:

1. Mild process conditions.
2. Carbon neutral.
3. For fuel the biomass is as close to the source as it gets. For chemical feedstocks the furanics are the ideal starting point.
4. Uses low upfront processing costs and is designed to be easily scaled.
5. Uses low cost and recyclable catalysts (e.g. iron based).
6. Would fit in the local economic model for regional production sites (100 mile radius).

Future work: Using $^{13}$C labeled carbohydrates to look at mechanistic aspects of oligosaccharide conversions – probing pathways by NMR and GC-MS.

Also probing details of “promiscuous” catalysts with respect to their ability to simultaneously hydrogenate different functional groups e.g. olefins and ketones (1st row transition metals).

Operated by Los Alamos National Security, LLC for the U.S. Department of Energy’s NNSA
Outputs so far

IP


SYMPOSIA
J. C. Gordon, L.A. "Pete" Silks, co-organizers with R. M. West (Procter and Gamble) and G. A. Kraus (Iowa State University); ACS National meeting, Denver, CO, Aug 2011, “Recycling Carbon: Catalyzed Conversion of Non-Food Based Biomass to Fuels And Chemicals”.

BOOKS

HOT TOPIC ISSUE
PAPERS


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