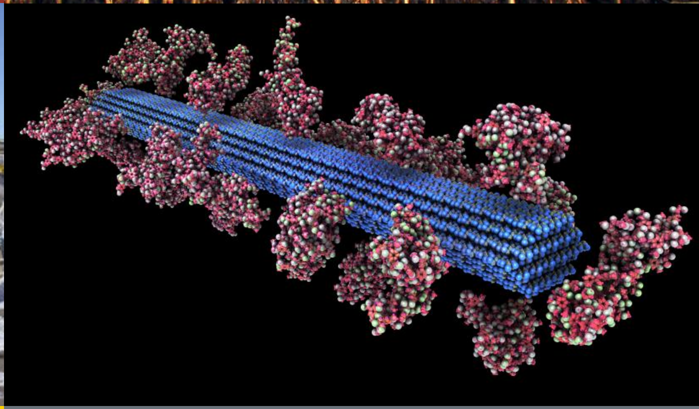
U.S. DEPARTMENT OF ENERGY BIOMASS PROGRAM

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy





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

December 12, 2012

Biomass Program Overview:

Lindsay Southerland, BCS, Incorporated, representing DOE

Hydrocarbon Presentation: Pete Silks and John Gordon, LANL

Biomass Program Vision, Mission, and Strategic Goal

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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

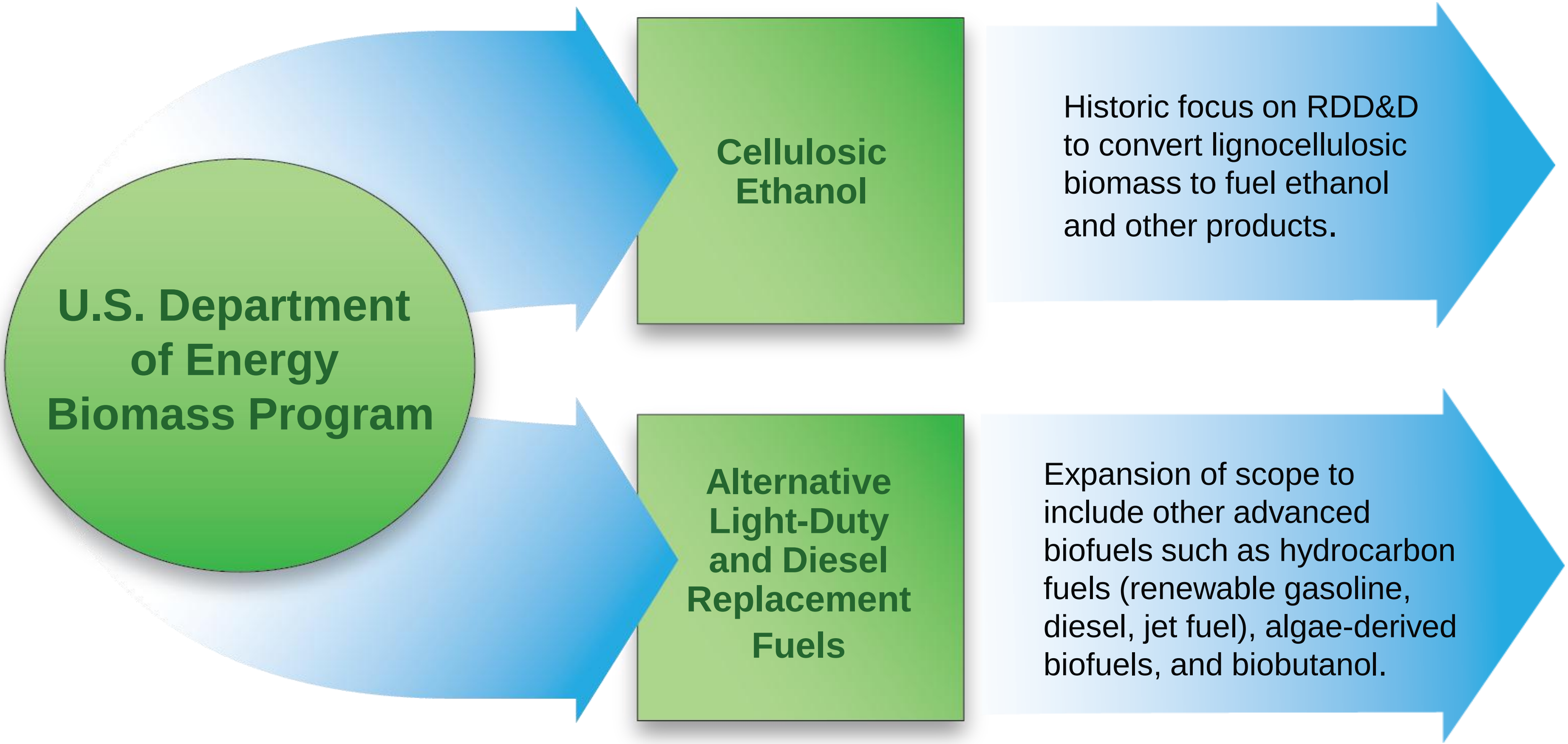
Develop and transform our renewable biomass resources into commercially viable, high-performance biofuels, bioproducts, and biopower through targeted research, development, demonstration, and deployment (RDD&D) supported through public and private partnerships.

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.

HOME

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.

HOME

The Role of Biomass

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1 The need to reduce dependence on foreign oil and lower GHG emissions has renewed the urgency for developing sustainable biofuels, bioproducts, and biopower.

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

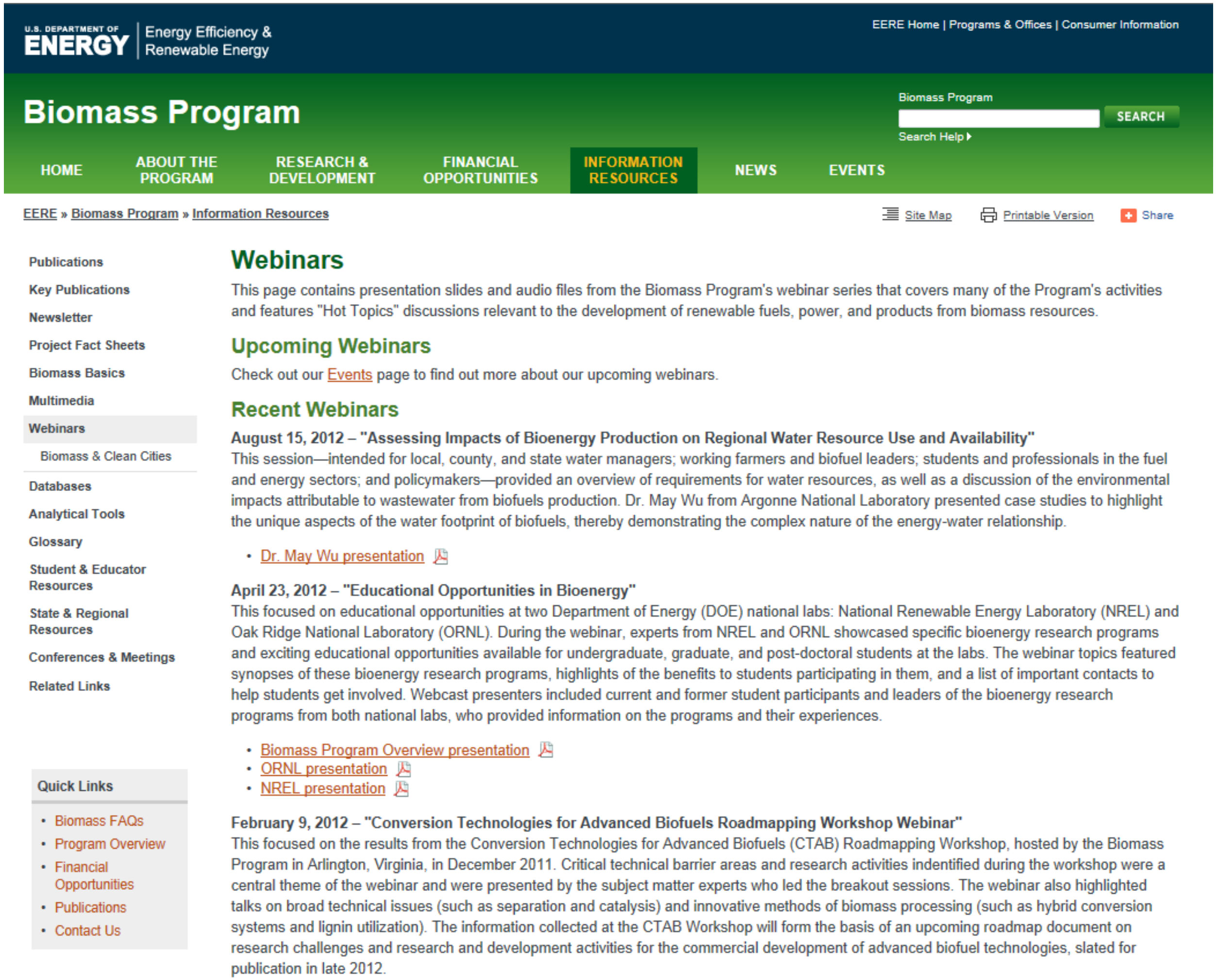
3 Near-term, biomass is the only renewable resource that can supplement petroleum-based liquid transportation fuels, while reducing GHG emissions.

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.

HOME

- 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

John Gordon and Pete Silks

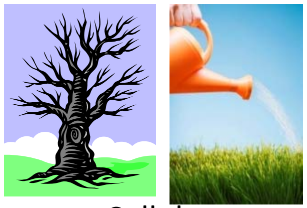
Los Alamos National Laboratory
Los Alamos, NM 87545

jgordon@lanl.gov and pete-silks@lanl.gov

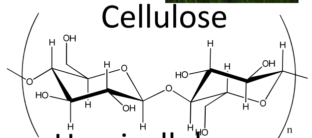
LA-UR-12-25668

Feedstocks

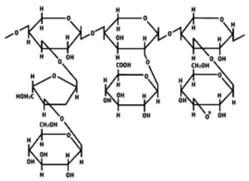
Wood Chips, Grasses
Stover / Husks, Sugars



Cellulose



Hemicellulose



Bio-Refinery

- Fermentation
- Dehydration / Acidic Treatment
- Hydrogen-based Treatments

Renewable Chemicals

Alcohols
Ethanol, Butanol
Acids/Esters
Levulinic, Acetic
Acrylic, Succinic
Ketones
Acetone,
Methyl-Vinyl
Furfurals
Hydroxy-Methyl,
Methyl,
Furfural

LANL direct catalytic carbon chain extension on oligosaccharides followed by HDO.

Hydrocarbon Fuels and Advanced Chemical Feedstocks

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

NOTE: Algal Starch has several advantages

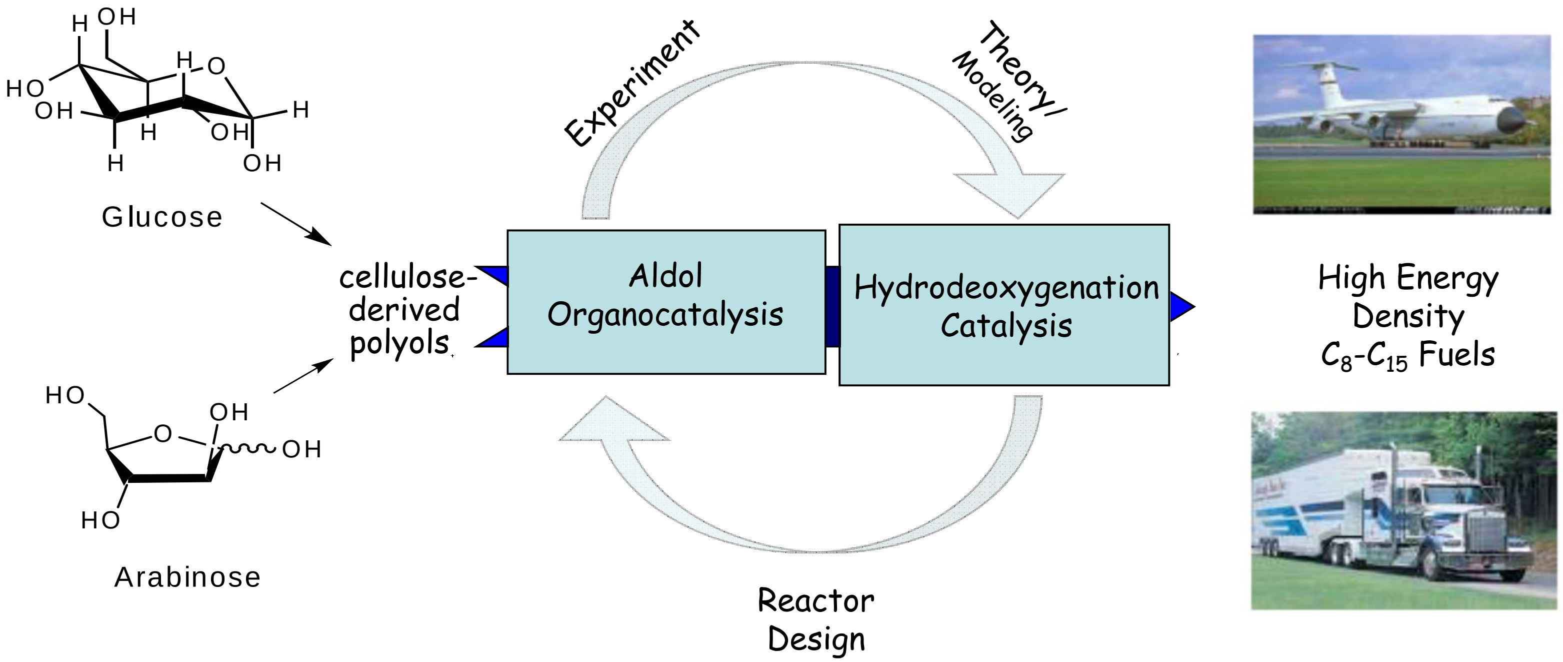
*** Companies such as Incitor are accessing furanics and levulinates from raw non-food based biomass with about ~10x decrease in current costs.**

*** 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.

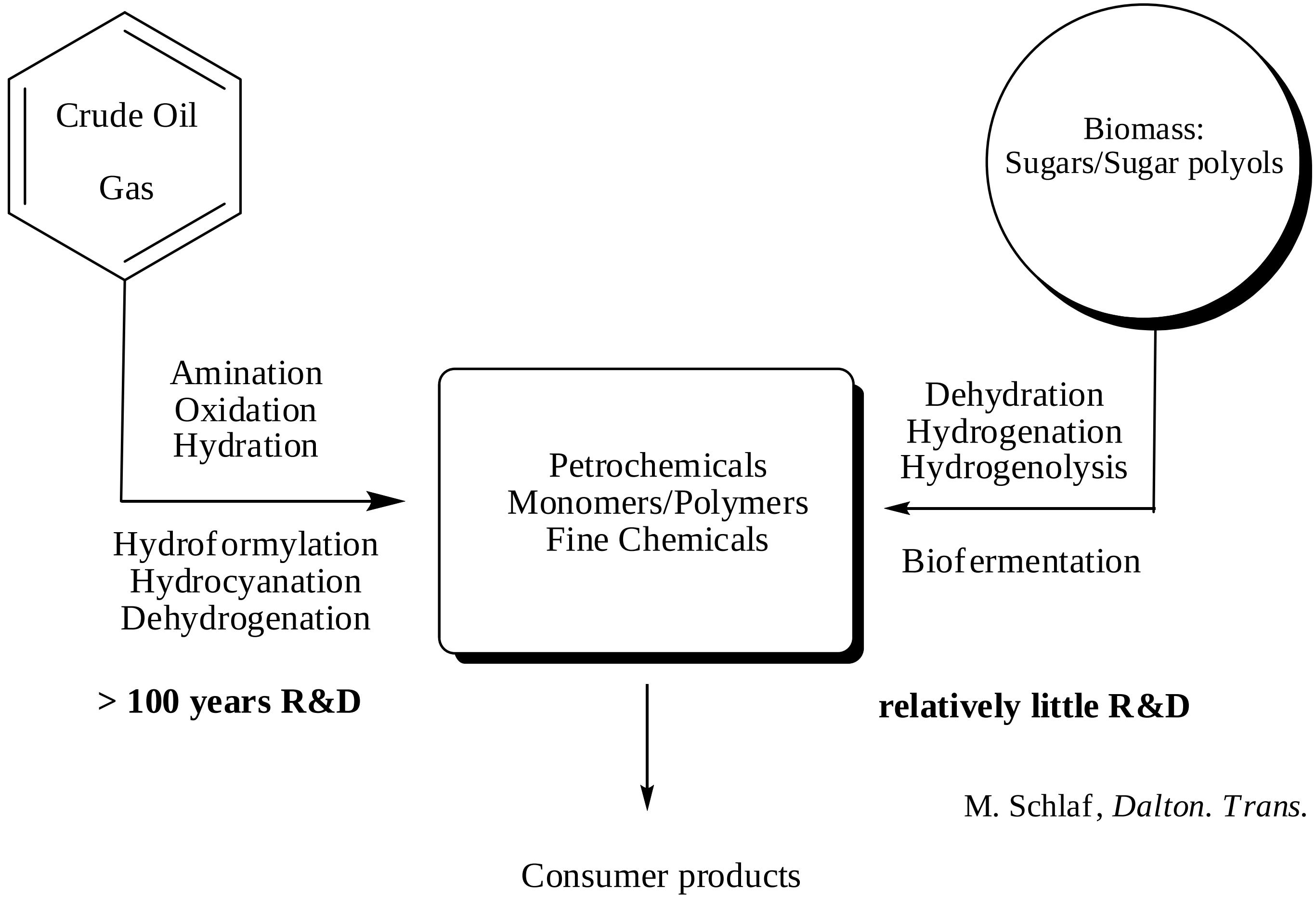
Funding from LANL LDRD & CRADA



The General Paradigm…

Low oxygen content
Underfunctionalization problem

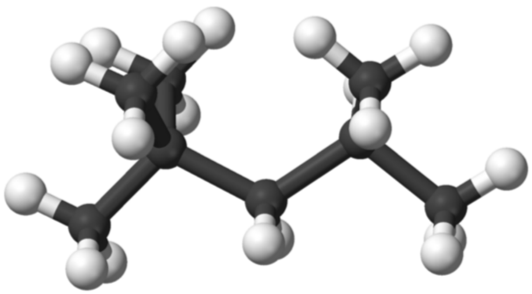
High oxygen content
Overfunctionalization problem



M. Schlaf, *Dalton. Trans.* **2006**, 4645

FACTS ABOUT FUEL-REMINDER

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………***

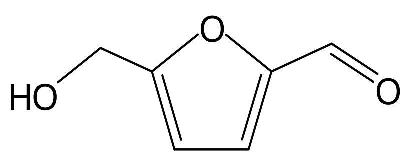
Petroleum-derived diesel is composed of about 75% saturated hydrocarbons. The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from approx. $C_{10}H_{20}$ to $C_{15}H_{28}$.

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.



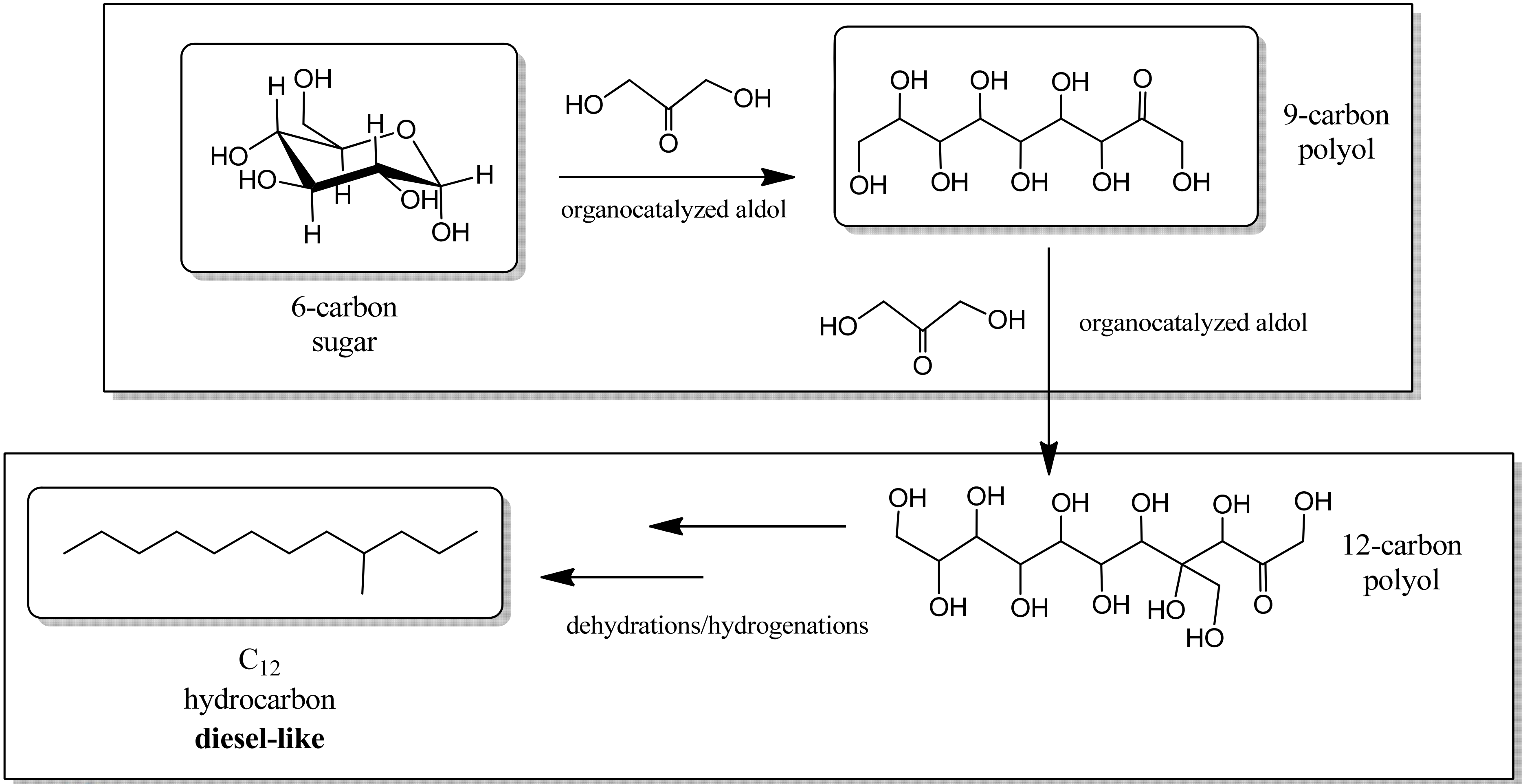
Hydroxymethylfurfural (HMF)
IUPAC: 5-(hydroxymethyl)-2-furaldehyde

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

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.*

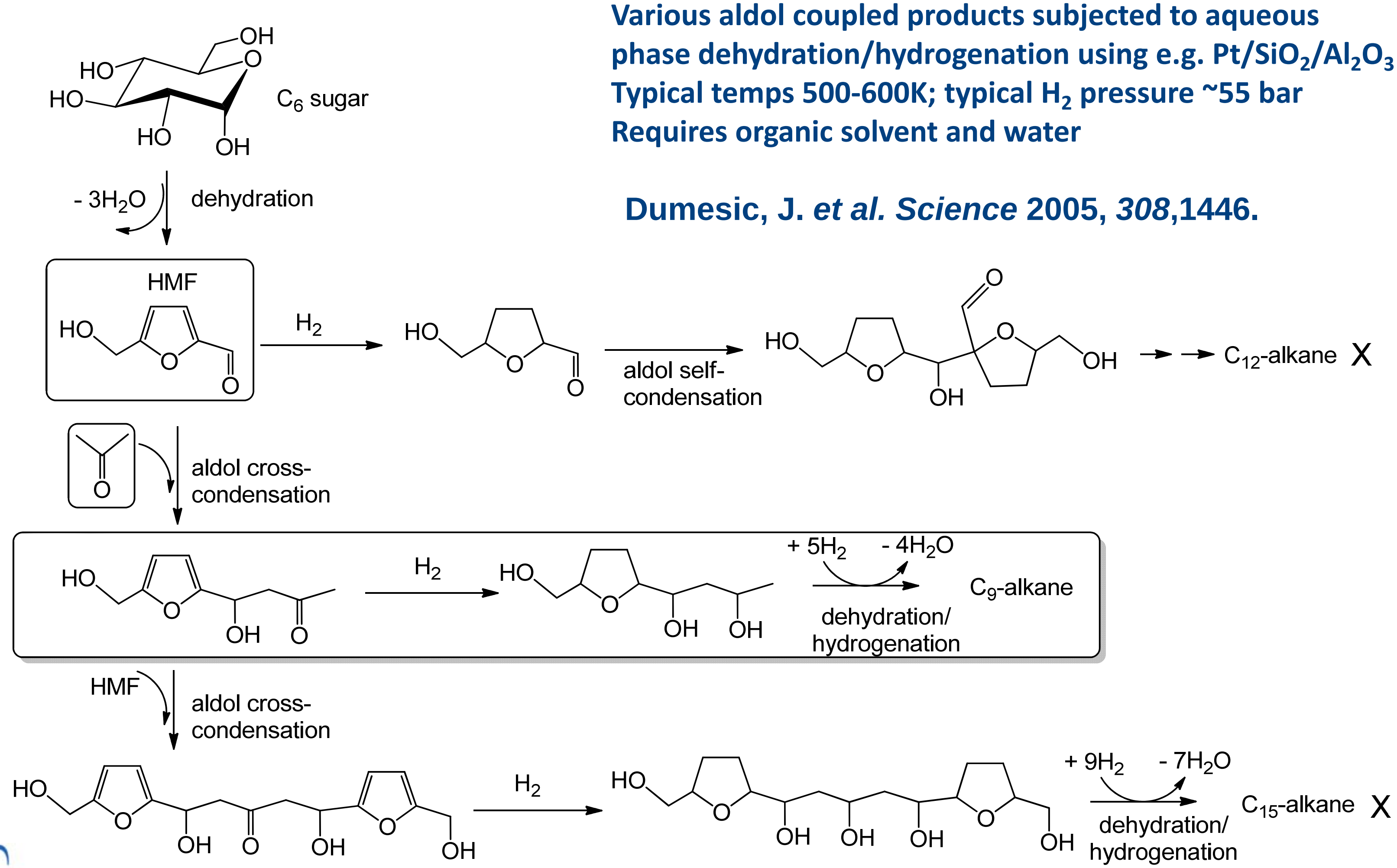
Synopsis of Initial Approach



Background: Feasibility Of Chain Extension Reactions Using *Bioderived* Synthons??

Various aldol coupled products subjected to aqueous phase dehydration/hydrogenation using e.g. Pt/SiO_2/Al_2O_3
Typical temps 500-600K; typical H_2 pressure ~55 bar
Requires organic solvent and water

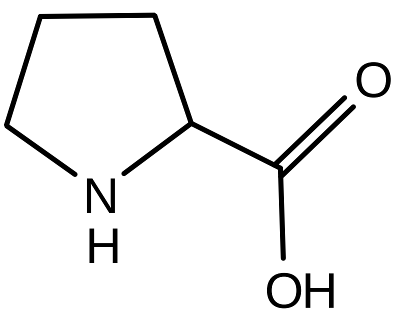
Dumesic, J. *et al. Science* 2005, *308*,1446.



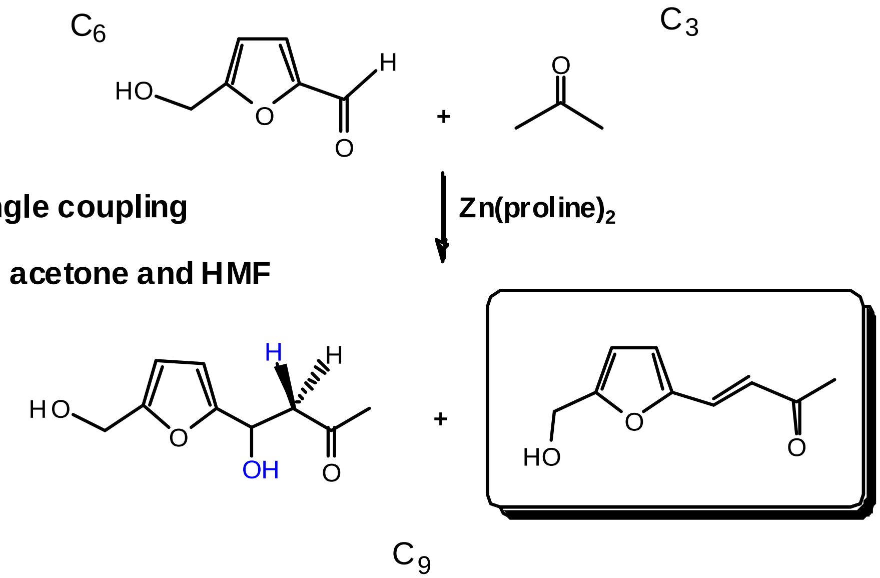
Our Starting Point for C-C Coupling:
Take Lesson from Nature: Aldolase Mimics..?

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-$^{13}C_3$]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..?

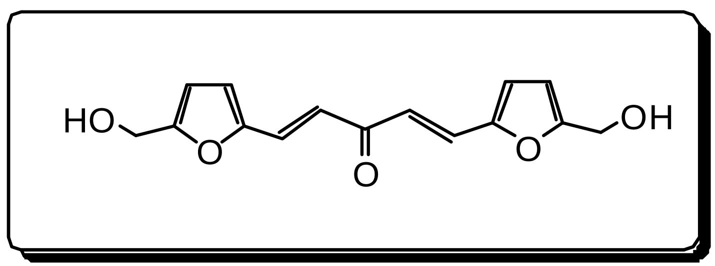


Single coupling

between acetone and HMF

can also get double coupling

(excess HMF)

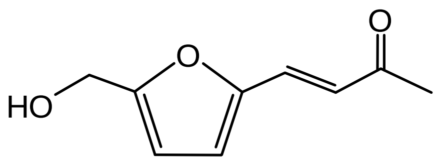


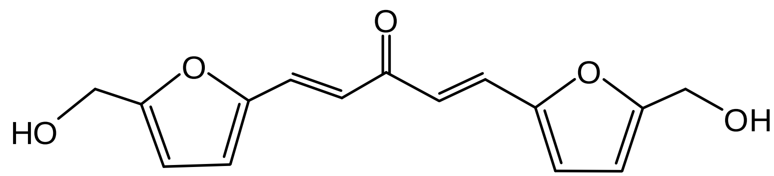
C_{15}

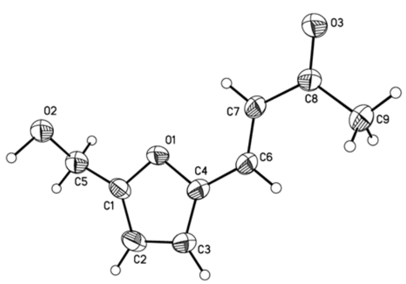
"Method of Carbon Chain Extension using Novel Aldol Reaction", US patent application 20110040110, filed August 17th, 2009.

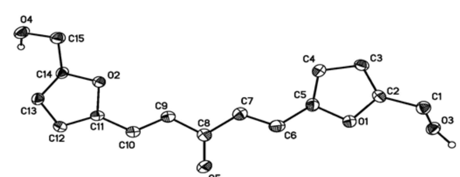
Piperidine as Catalyst for C_9 and C_{15} Fragment Syntheses (100 g quantities)…!!!

HMF + Acetone; in water, at ambient temperature, overnight



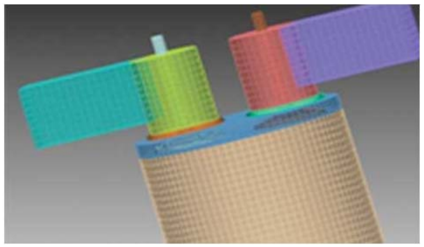




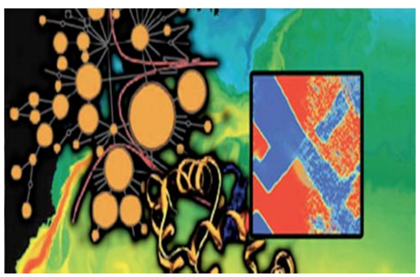


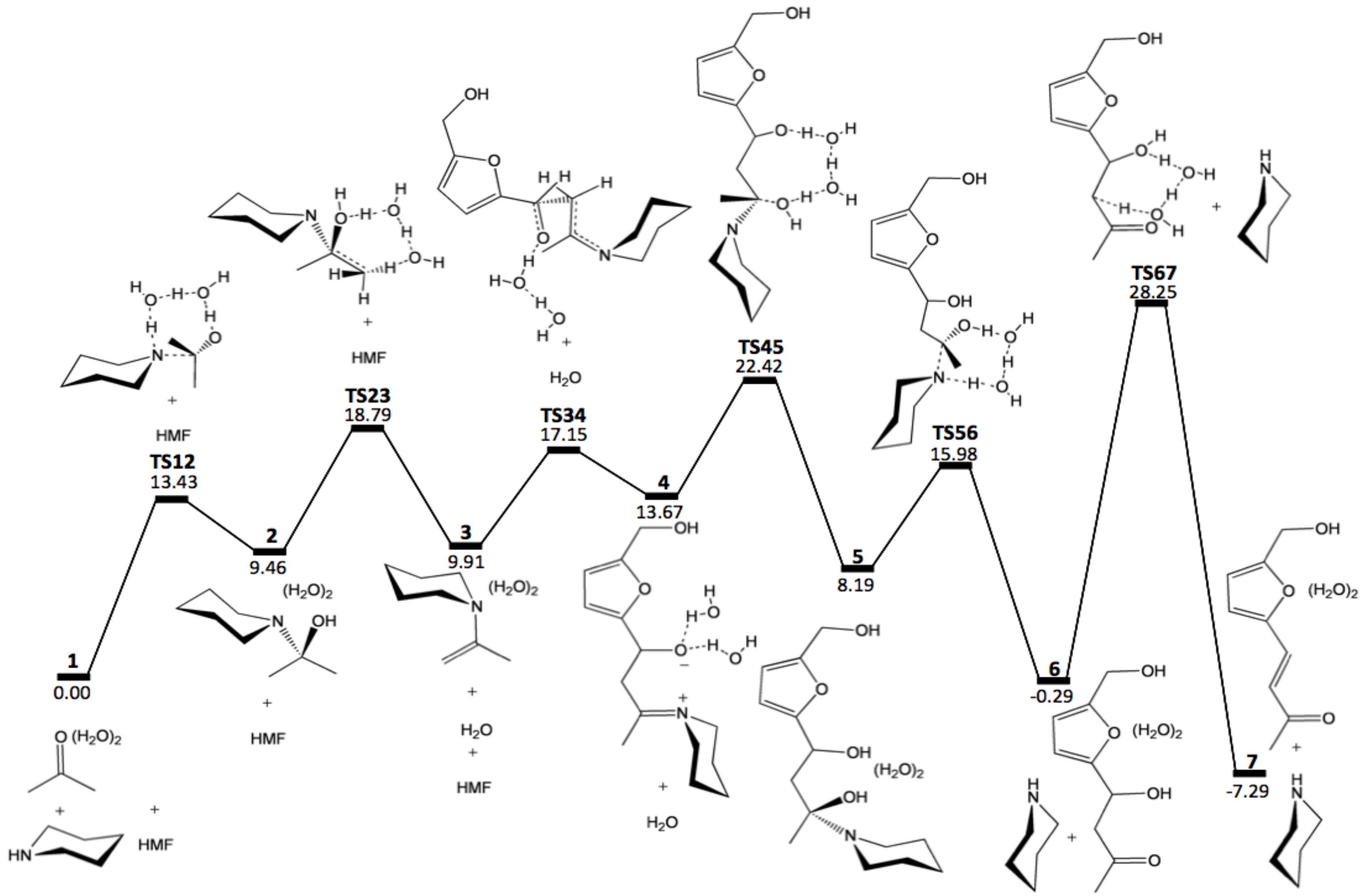
Piperidine as Catalyst for C_9 and C_{15} Fragment Syntheses: Water Orders Transition State (LANL Capabilities Leveraged)

Theoretical Division



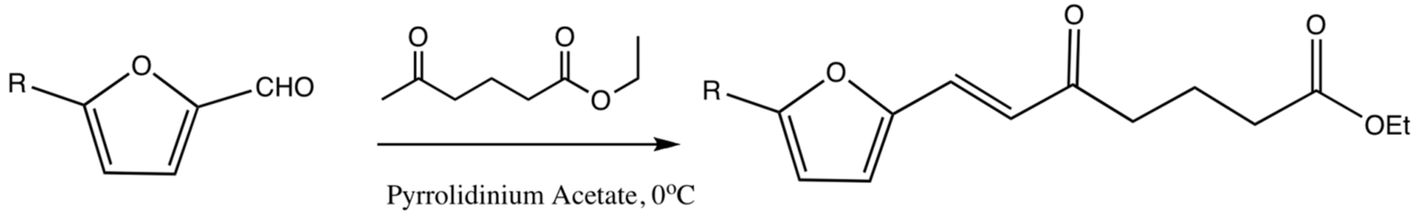
Center for Nonlinear Studies





Keith, J. M., Kim, J. K., Alexander, L., Wu, R., Martin, R. L., Batista, E. R., Michalczyk, R., Scott, B., Hanson, S. K., Sutton, A. D., Gordon, J, C., Silks, L. A. P., "Aqueous Organocatalysis Applicable to the Carbon Chain Extension of Carbohydrate Derivatives: Application to the Production of Transportation Fuels" *Current Organic Chemistry* **2012**, accepted.

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



$R = CH_3, CH_2OH$

Linear C_{12} Unit

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 Appiications. NOTE: both process and composition of matter covered.

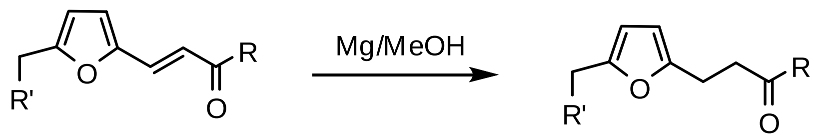
Converting Aldol Products into Alkanes

Steps required:

- **Ring opening of furans**
- **Hydrogenation of olefins**
- **Hydrodeoxygenation of ketones**

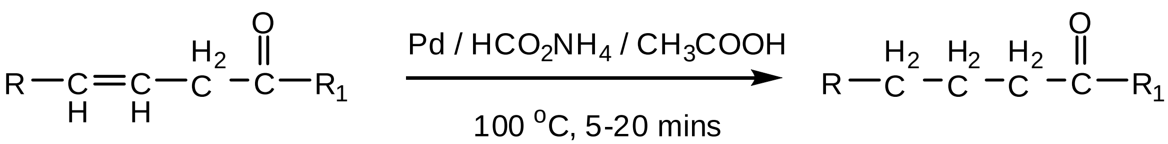
Interrogation of Aldol Derived C_9 Precursor as Model System

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



R = H, alkyl
R' = OH, H

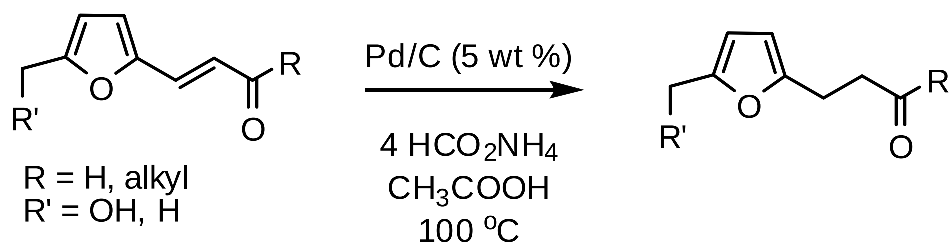
50 – 60 % isolated yield



R = H, alkyl, aryl, $-CO_2C_2H_5$
R_1 = $-OC_2H_5$, $-NH_3$, $-CH_3$, $-CH{=}CHC_6H_5$

64 – 93 % isolated yield

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

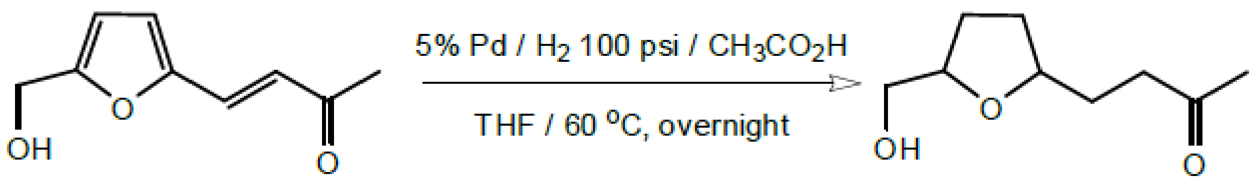


~ 85 % isolated yield

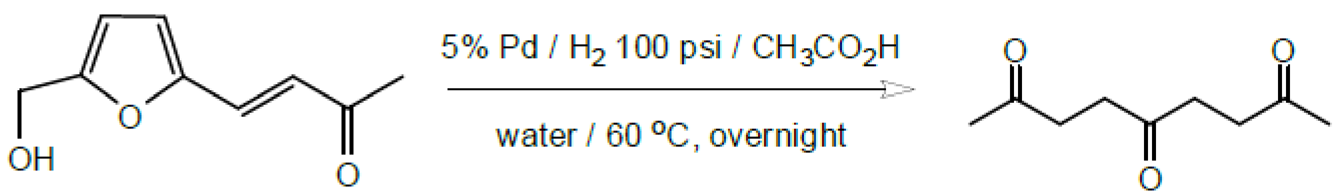
Moved to Pressurized Systems with H_2

Following H-transfer reagents, move to H_2 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 (H_2 uptakes) and Product Yields?

Reservoirs allow H_2 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

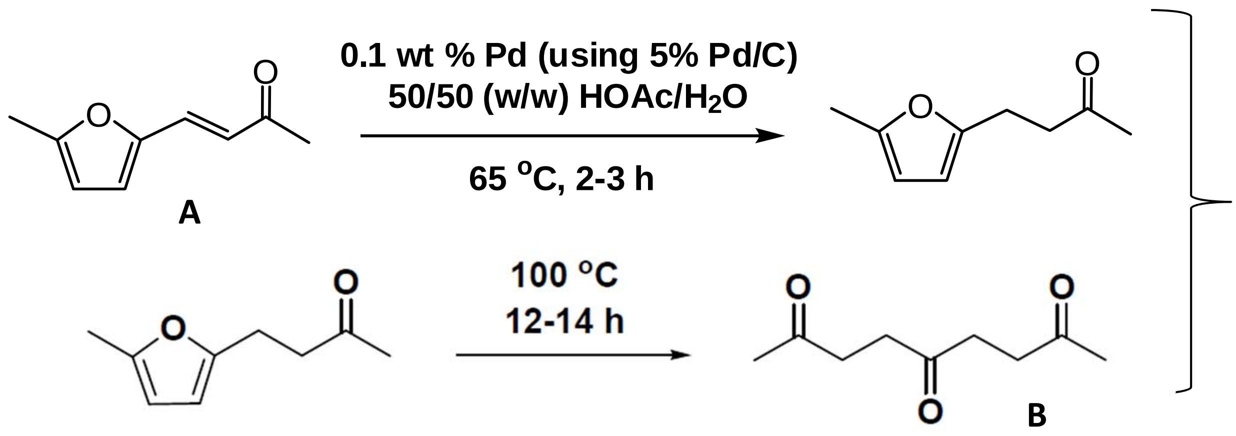
Max. operating pressure = 1500 psi

Max. temp. = 250 °C

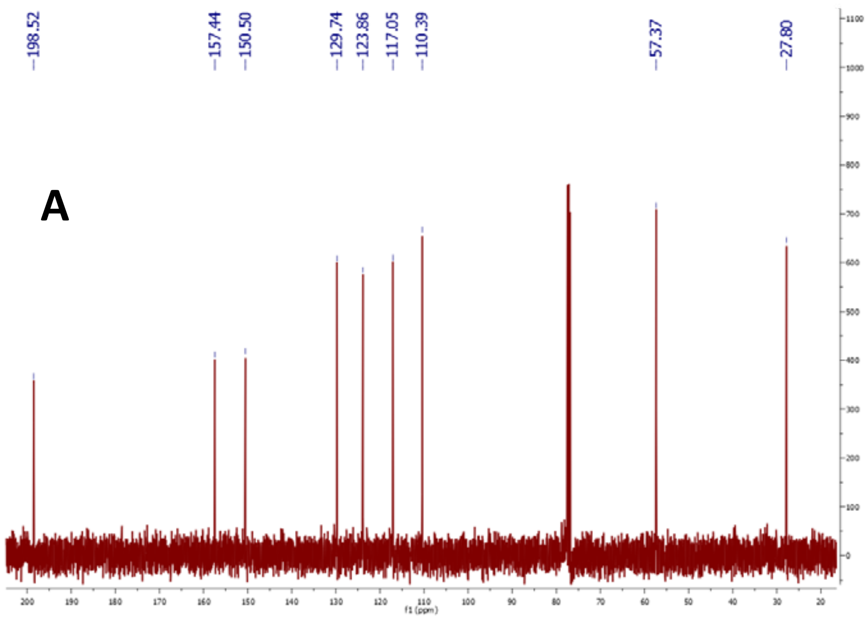
Head space and solution samples removed after hydrogenation for analysis by GC-MS

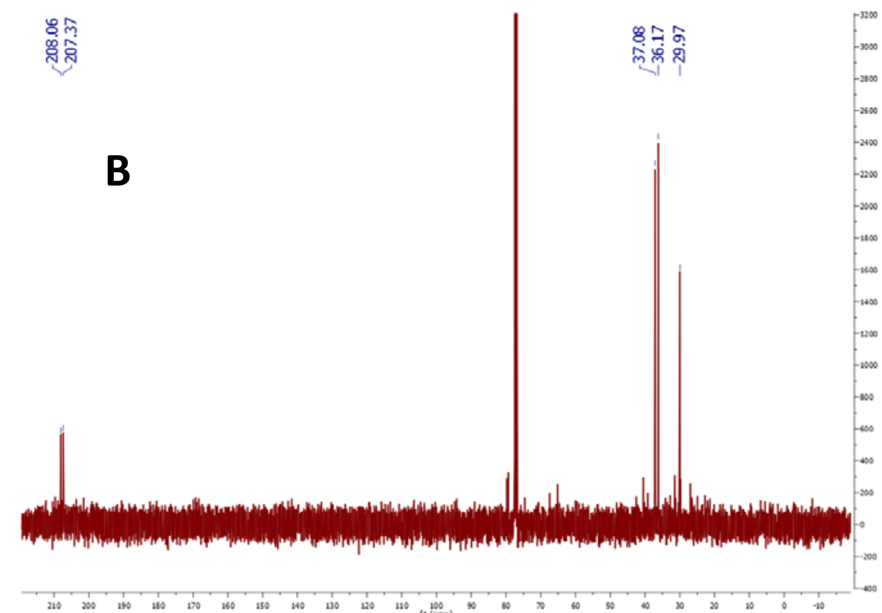
Marcel Schlaf, Fraser Waldie, U. Guelph

Further Refinement – Multi-Step (w/U.Guelph)

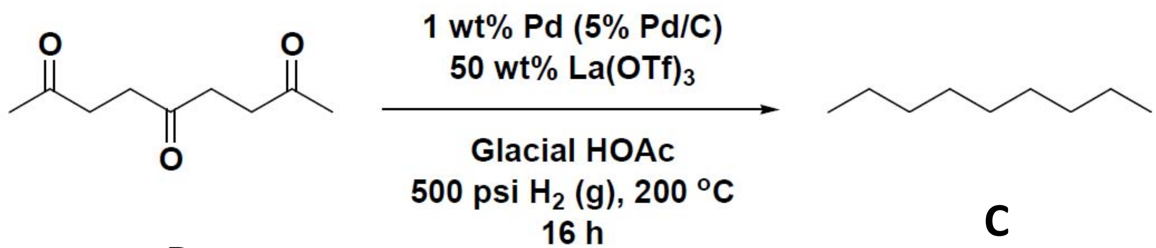


Up to 98 % isolated yield



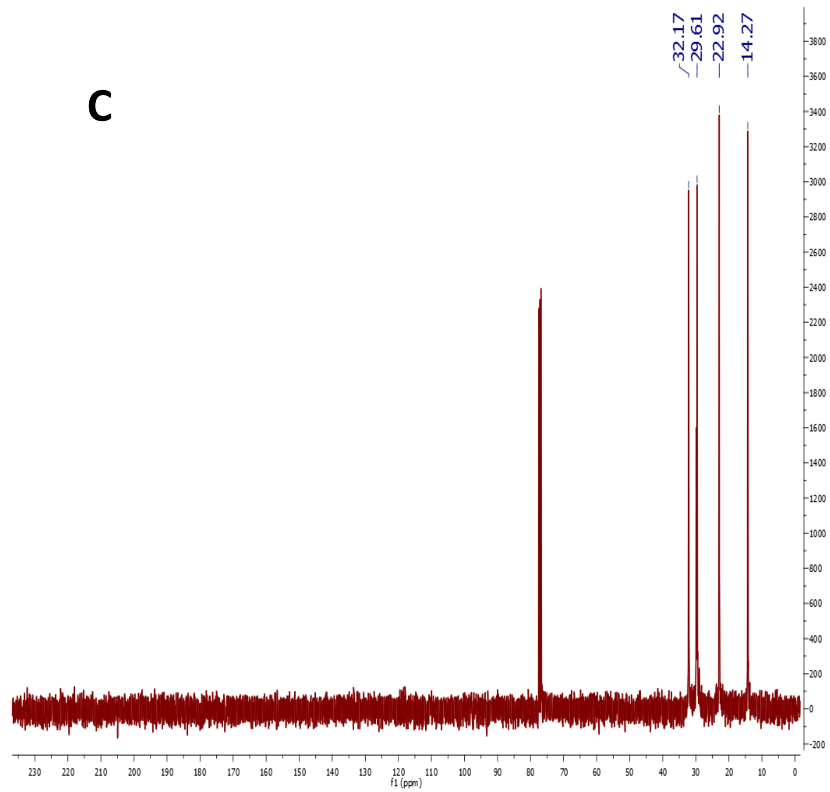


Then isolated Triketone to Nonane



B

C



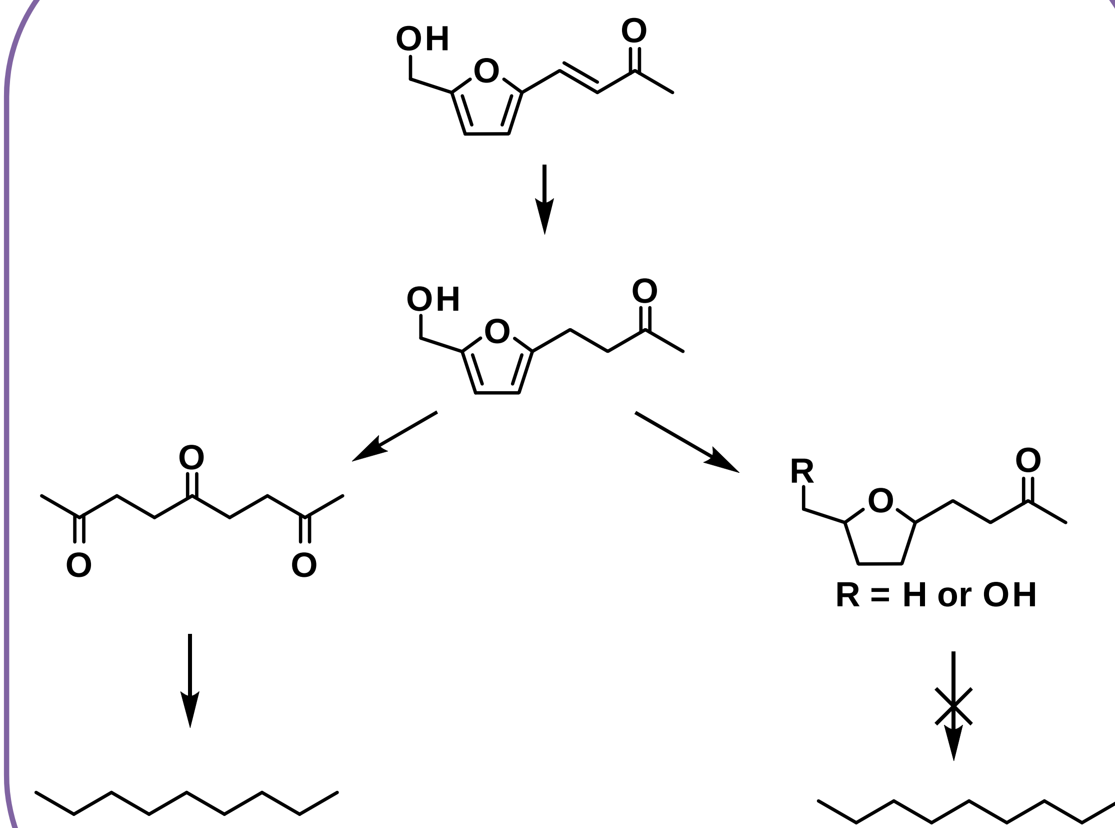
One Product (GC-MS):
6 eq. H_2 taken up
100 % conversion

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

Possibly coking for the remaining 10%,
Minimal CO_2 in headspace

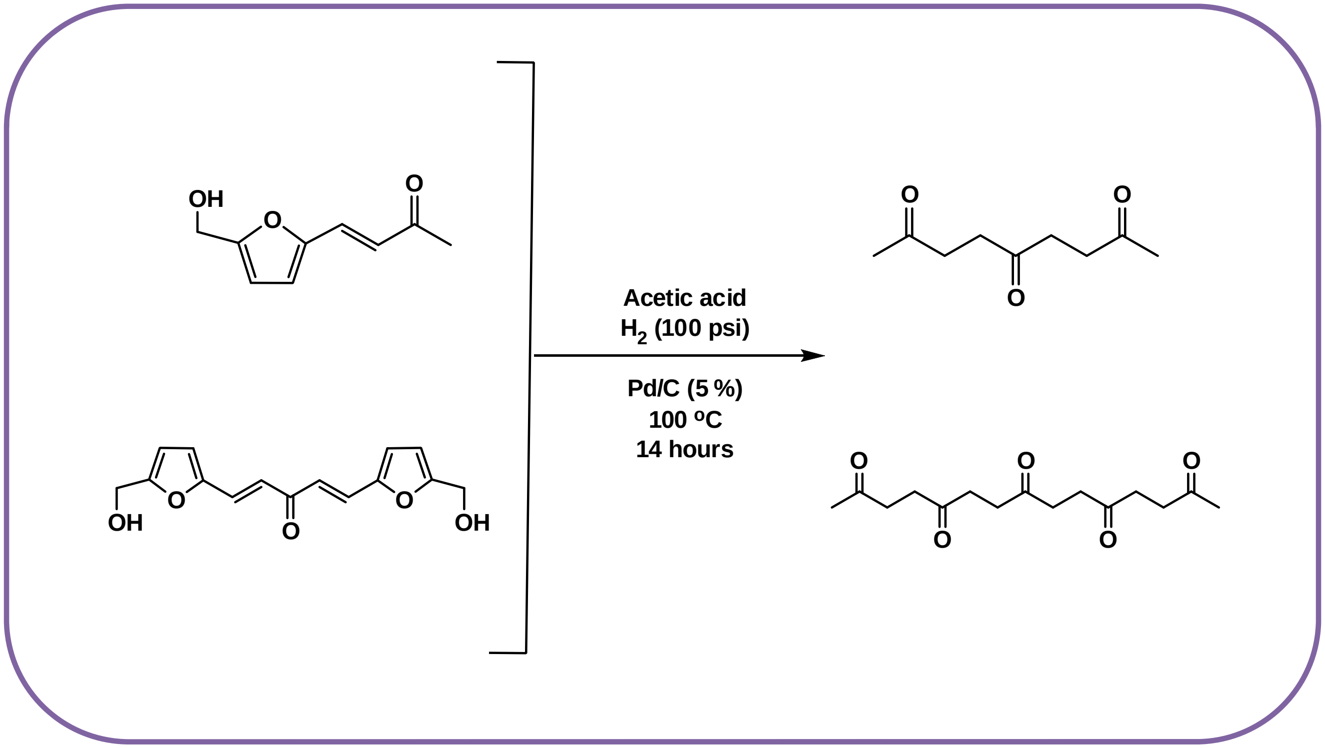
C_9 Reaction Pathway

- 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_2 pressure favors ring hydrogenation



Chemistry Generally Applicable to Other Chain Lengths

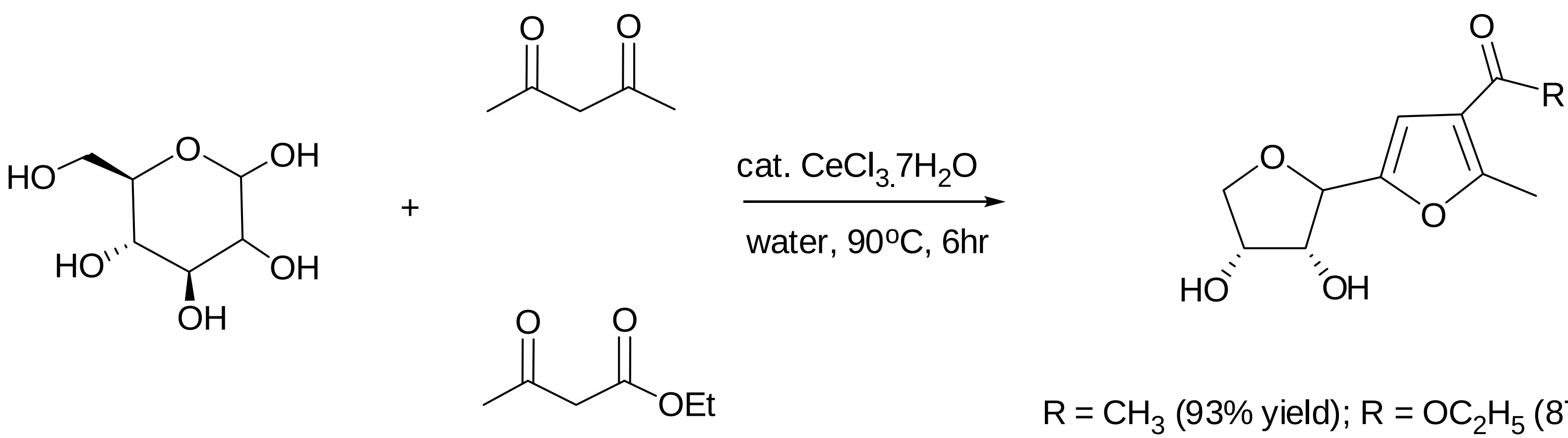
Method is general to generate other polyketones, which can then be subjected to HDO to make array of alkanes *UNDER MILD CONDITIONS*….



Waidmann, C. R., Pierpont, A. W., West, R., Batista, E. R., Gordon, J, C., Martin, R. L., Silks, L. A. P., Wu, R.,:
"Catalytic Ring Opening of Furan Rings Within Biomass Derived Substrates: An Experimental and Theoretical Study"

Catalysis Science and Technology **2012**, *Hot Article* (asked to submit cover graphics)

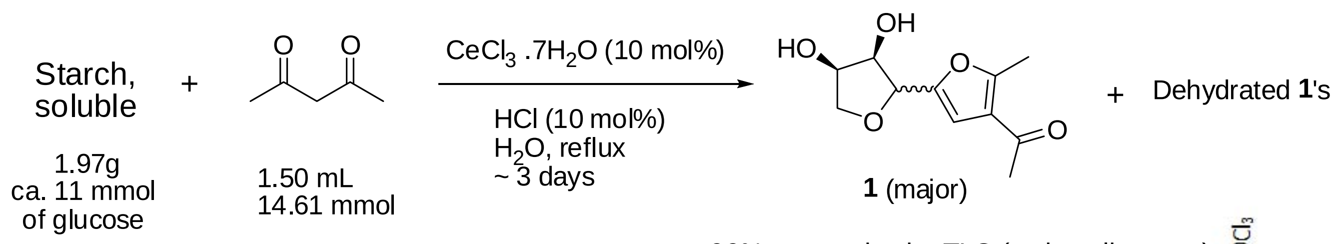
What About Alkanes Directly from Sugars?



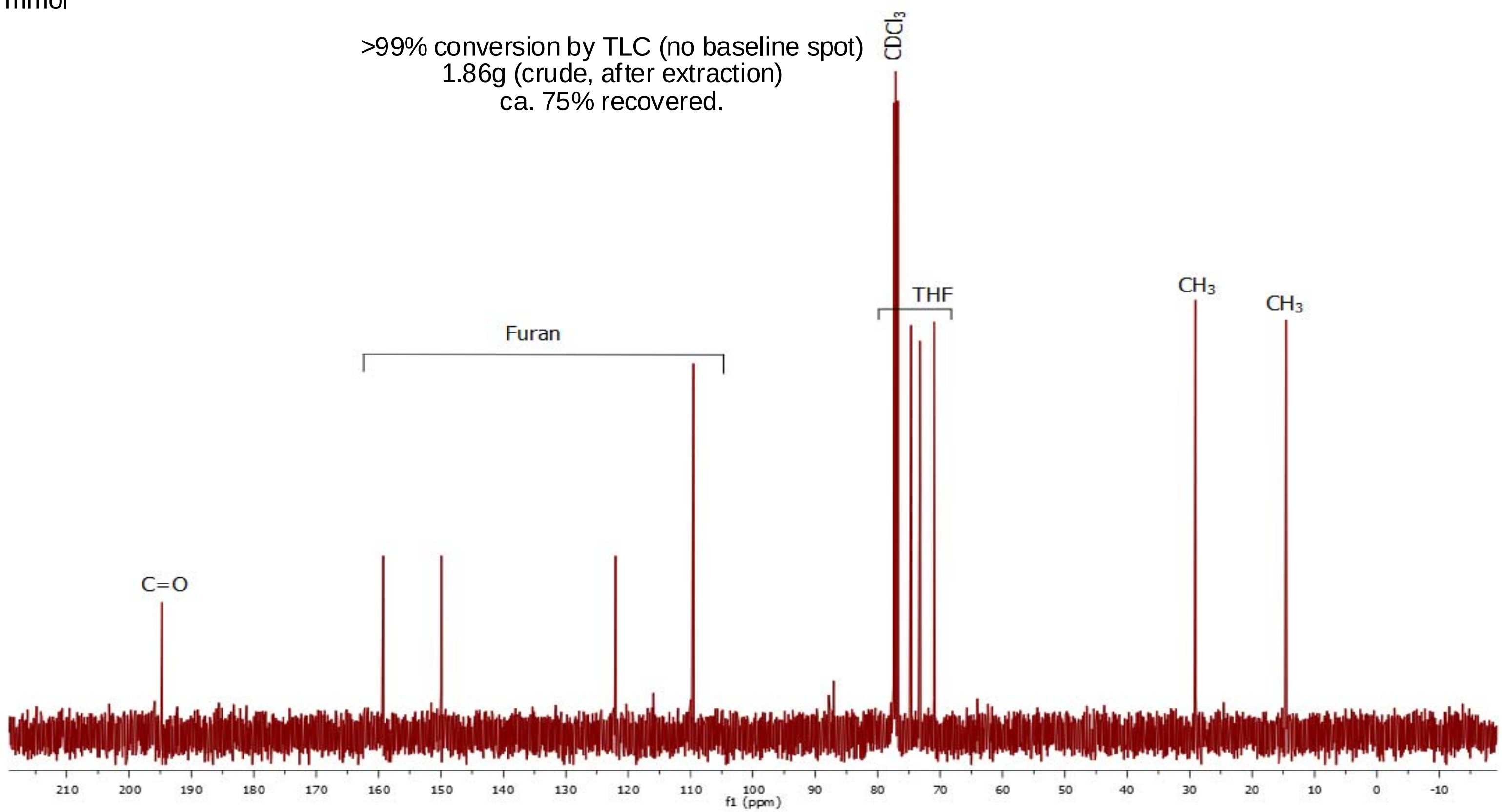
R = CH_3 (93% yield); R = OC_2H_5 (87% yield)

Misra, A. K. ; Agnihotri, G. *Carbohydrate Research* **2004**, *339*, 1381

Undressing Algal Starch: Two Step Process to Hydrocarbons



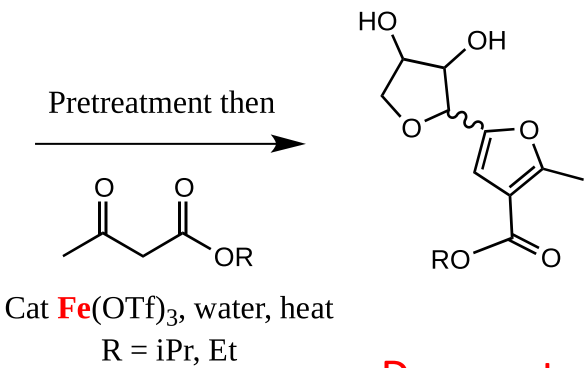
>99% conversion by TLC (no baseline spot)
1.86g (crude, after extraction)
ca. 75% recovered.



Undressing Algal Starch: Two Step Process to Hydrocarbons

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

Glucose

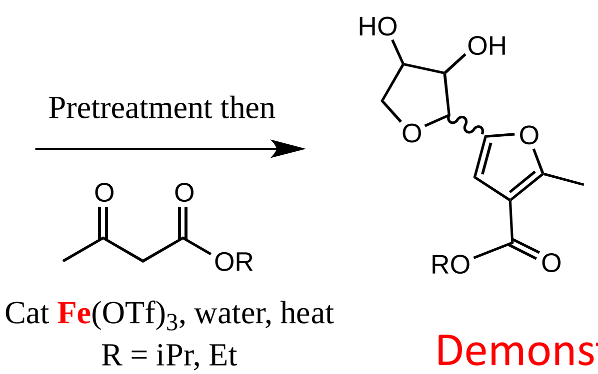


Three cycles
74%, 90%, 95%

Demonstrates catalyst activity
Is inert to reuse.

Completed reaction upon Cooling. Biphasic: Easy Separation and offers simple flow through reactor set-ups.

Algal or Potato soluble starch

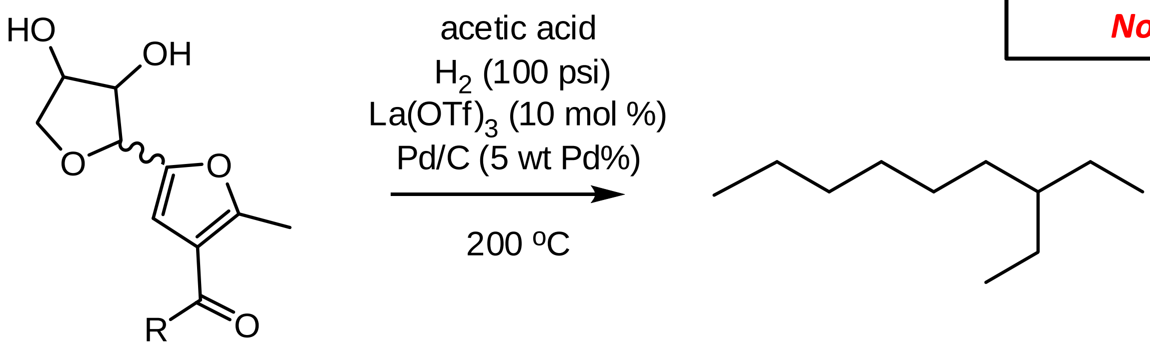


~74%

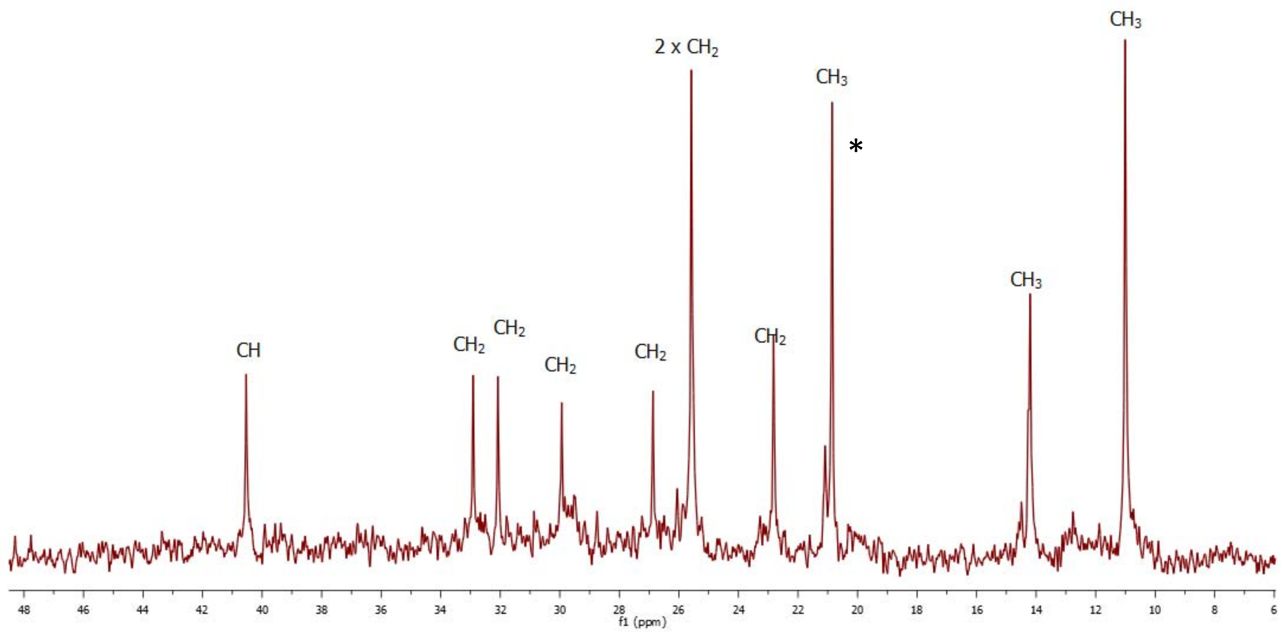
Demonstrates similar activity using starch compared to glucose.

HDO on GG Product to Give Branched Hydrocarbons

Other potential oligosaccharide sources include cellulose, hemicellulose, cotton, and chitin.
Note: <u>Starch from Algae is Lignin free</u>

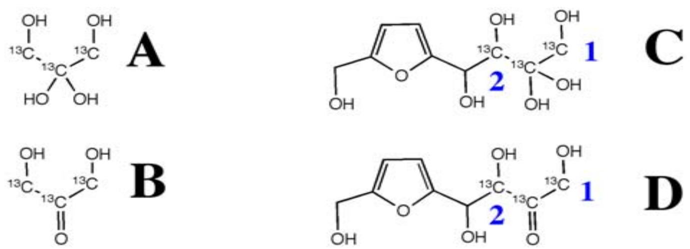


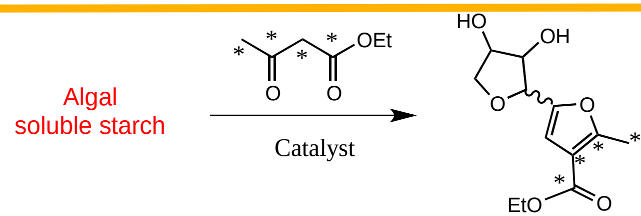
R = CH_3



Leveraging LANL Stable Isotope Resource Capabilities: Synthesis of Labeled Precursors Readily Allows the Interrogation of Reaction Pathways and Easy Optimization of Conditions

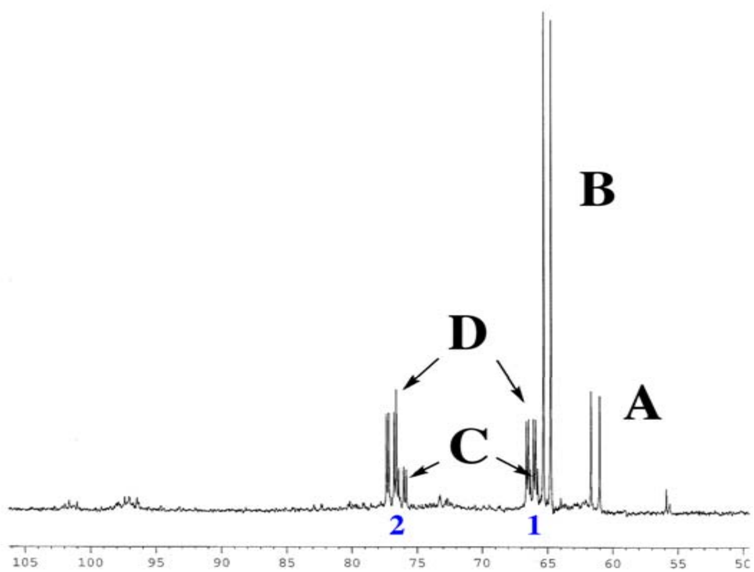
Organocatalyzed reaction of $[1,2,3\text{-}^{13}C_3]$DHA + HMF



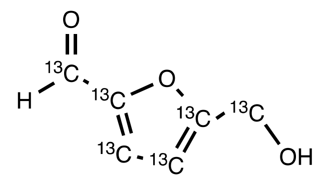


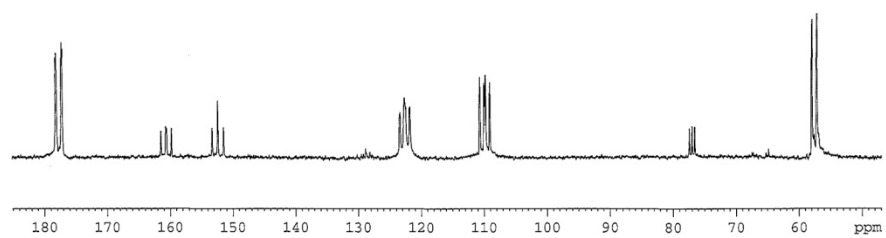
greater than 95% conversion

Use mass spectrometry to
Quickly assess reaction status

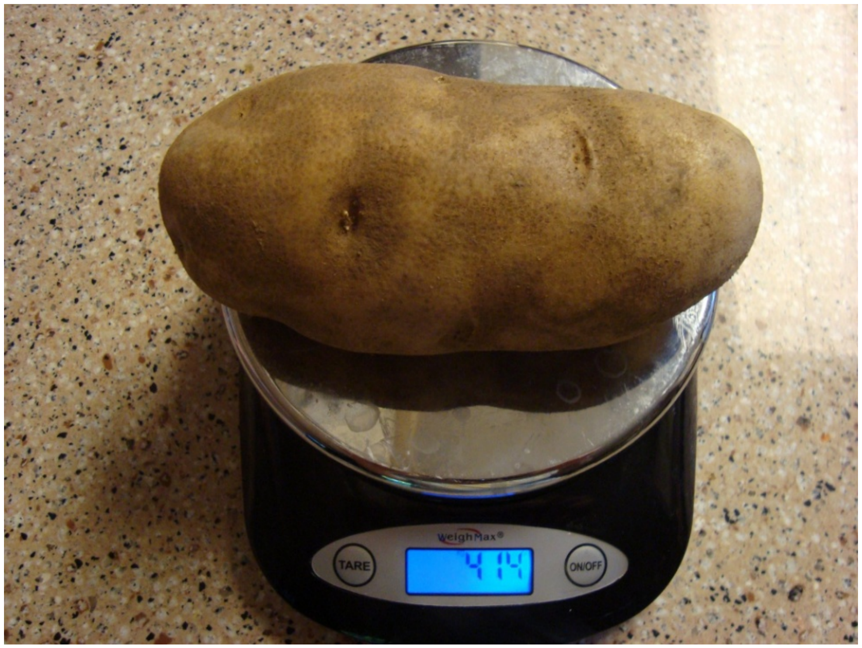


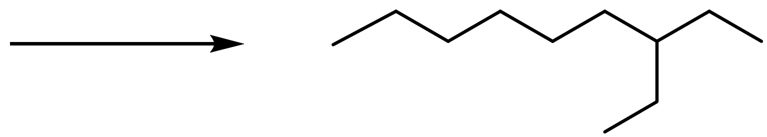
^{13}C labeled HMF from Glucose using Lanthanide Catalyst $(Yb(OTf)_3$, 10%, in water) i.e. integrates *dehydration chemistry in water with isotope labeling*





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).

Outputs so far

IP

"Method of Carbon Chain Extension using Novel Aldol Reaction", US application 20110040110, filed August 17th, 2009.

"Method of Carbon Chain Extension using Novel Aldol Reaction", US application 20110040109, filed August 17th, 2009.

"Compounds and Methods For the Production of Long Chain Hydrocarbons From Biological Sources", 1st US Provisional Patent Application No. 61/534,496, filed September 14th, 2011; 2nd US Provisional Patent No. 61/669,775, filed July 10th, 2012.

"One Step Conversion of Oligomeric Starch or Cellulose to Single C_{10} or C_{11} Carbon Chains Furans and their Conversion to Fuel Hydrocarbons", US Provisional Patent Application No. 61/669,980, filed July 10th, 2012.

"Compounds and Methods for the Production of Long Chain Hydrocarbons From Biological Sources", International Patent Application No. PCT/US2012/055340 filed Sept. 14, 2012 (claiming priority of US provisional Application nos. 61/534,496, filed Sept. 14, 2011 & 61/669,775, filed July 10, 2012).

"Conversion of Oligomeric Starch, Cellulose or Sugars to Hydrocarbons", International Patent Application No. PCT/US2012/055337 filed Sept. 14, 2012 (claiming priority of US provisional application no. 61/669,980, filed July 10, 2012).

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

J. C. Gordon, L.A. "Pete" Silks - asked to co-edit text book on Catalysis for Renewable and Sustainable Energy Applications, John Wiley and Sons.

HOT TOPIC ISSUE

Current Organic Chemistry: "Biomass to Fuels and Chemical Feedstock. L.A. "Pete" Silks, Editor.

PAPERS

J. M. Keith, J. K. Kim, L. Alexander, R. Wu, R. L. Martin, E. R. Batista, R. Michalczyk, B. L. Scott, S. K. Hanson, A. D. Sutton, L. A. Silks, J. C. Gordon: "Aqueous Organocatalysis Applicable to the Carbon Chain Extension of Carbohydrate Derivatives: Application to the Production of Transportation Fuels", *Current Organic Chemistry*, **accepted.**

Waidmann, C. R., Pierpont, A. W., West, R., Batista, E. R., Gordon, J, C., Martin, R. L., Silks, L. A. P., Wu, R., "Catalytic Ring Opening of Furan Rings Within Biomass Derived Substrates: An Experimental and Theoretical Study" *Catalysis Science and Technology* **2012**, online, DOI: 10.1039/C2CY20395B, ***selected as a Hot Article.***

Sutton, A. D., Waldie, F., Wu, R., Schlaf, M, Silks, L. A. P. Silks, Gordon, J. C. "The Hydrodeoxygenation of Bioderived Polyols into Alkanes," *Nature Chemistry* **2012**, submitted, under review.

Wu, R., Silks, L. A. P., Gordon, J. C. "Carbon Chain Extension of Carbohydrate Derivatives: Solventless Carboxylic Anhydride Additions to Furans." For submission to J. Am Chem. Soc. Model Systems Studies of Starch Conversion to Biofuel via Garcia-Gonzales and HDO Reactions"": J. K. Kim, L. A. Pete Silks III, J. C. Gordon, R. Wu, A. D. Sutton. For submission to *Science.*

J. K. Kim, W. Chen, J. C. Gordon, R. Michalczyk, L. A. Silks III, A. D. Sutton, R. Wu: "Stereoselectivity in Lanthanide Catalyzed Synthesis of Acetals and Ketals from Biorenewable Polyols", for submission to *ChemSusChem.*

C R. Waidmann, A. W. Pierpont, J. C. Gordon, R. L. Martin: "Reductions of Olefins and Ketones in Biomass Derived Substrates Using Air stable Copper Catalysts at Room Temperature", *ChemComm* submitted.

Alexander, L., Wu, R., Silks, L. A. P., Kim, J. K., Gordon, J. C. "Soventless and Selective Organocatalyzed Aldol Reactions of Biomass Derived Furan Aldehydes with Levulinates: For High Energy Density Fuel Production." for submission to *Angew. Chem. Int. Ed. Eng*

Keith, J. M, Wu, R., Silks, L. A. P., Gordon, J. C. , Martin, R. L., Batista,E. R. "Modeling Solventless Organocatalyzed Coupling of Carbohydrate Derivatives for Fuel Production." For submission to *J. Am. Chem. Soc.*

Wu, R., Kim, J. K., Silks, L. A. P., Gordon, J. C. "Carbon Chain Extended Biomass Derived Carbohydrates: Addition of Three and Four Carbon Units to Furans for Hydrocarbon Fuel Production." For submission to *Chem omm.*

Wu, R., Kim, J. K., Silks, L. A. P., Gordon, J. C. "Using the Marita-Baylis-Hillman Reaction for Carbon Chain Extension of Carbohydrate Derivatives." For submission to *Synthesis.*

Acknowledgements

Organocatalysis

Lisa Alexander, Caroline Hoyt, Jin Kim, Ruilian Wu, Ryszard Michalczyk, Pete Silks

Ryan West (Procter and Gamble)

Oxygen Atom Removal and Hydrogenation Catalysis

Weizhong Chen, Robert Currier, Rico Del Sesto, Matt Dirmyer,
Matt Jones, Andy Sutton, Felicia Taw, Ryan Trovitch, Chris Waidmann

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Uttam Das, Steve Maguire

CCRI CRIC Center for Catalysis Research and Innovation / Centre de Recherche et d'Innovation en Catalyse

Theory/Mechanism

Enrique Batista, Jason Keith, Rich Martin, Aaron Pierpont

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