

# Electrocatalytic Upgrading: Opportunities and Challenges

ARPA-E Workshop  
“Rewiring Anaerobic Digestion”

27 Oct 2016  
Washington DC



# James E. “Ned” Jackson

## Department of Chemistry, Michigan State University



**NJ Bio:** Professor of Chemistry  
A.B. Harvard '77; Ph.D. Princeton '87;  
PD Ohio State '86-8; MSU '88-present  
*Organic reaction mechs, Green chem/catalysis,  
Design of molecular materials & interactions,  
Quantum chem modeling & electronic structure*  
~118 pubs, 15 pat, 18 PhDs, 6 MS, ~100 UG+HS

**Centers + Collaborators:** “SETS-UP” w/ Gail Richmond, GLBRC (DOE), Pharm/Tox

- Chem. engineers Miller, Saffron, Lira on catalysis, bioenergy, solution thermochem
- Borhan on organocat synthesis devel (NSF)

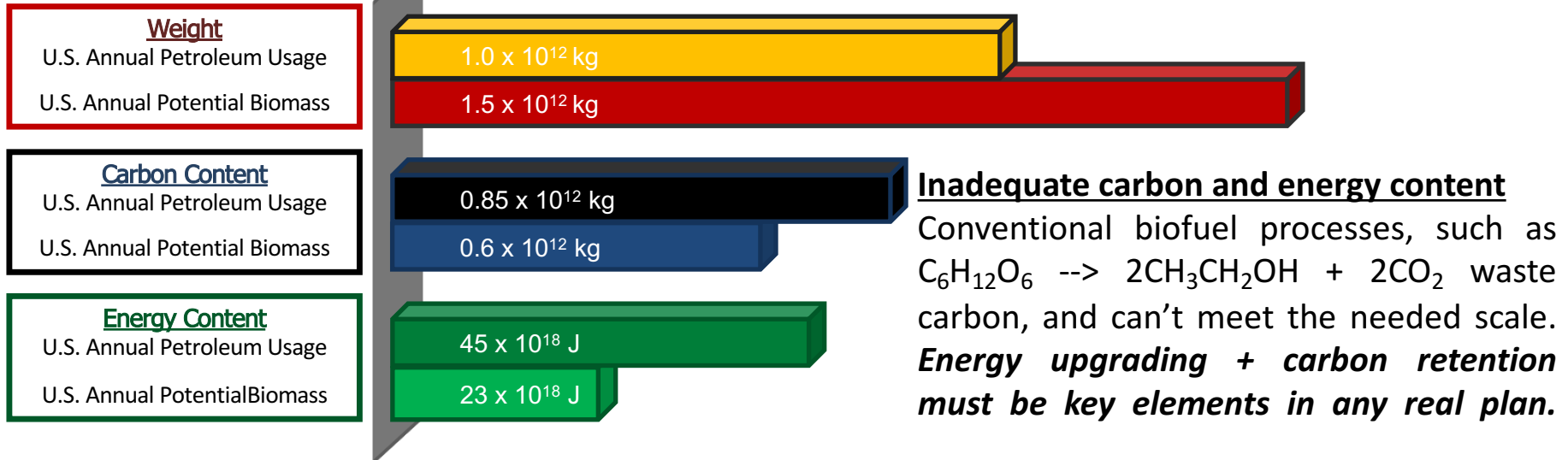
### **Technology Overview:**

- Liquid hydrocarbons will remain key fuels as nature (adipose tissue) implies
- Simple biomass-to-fuel lacks adequate energy (**E**) & carbon (**C**) scales
- Plants: poor at capturing **E**, best at capturing **C**
- Humans: poor at capturing **C**, better at (solar/wind) **E**, but all in form of electricity
- So, use PV/wind **E** to energy-upgrade biomass **C** to hydrocarbons via electrocatalytic hydrodeoxygenation, avoiding three-phase ( $\text{H}_2$  gas/ $\text{H}_2\text{O}$  liquid/solid electrocatalyst) barriers
- Feedstock may derive from all forms of biomass liquefaction treatment (AFEX, pyrolysis, AHP, etc.). Hydrophobic organic electroreduced layer may be skimmed
- Electrocatalysis offers wide opportunities for novel “green” reaction discovery

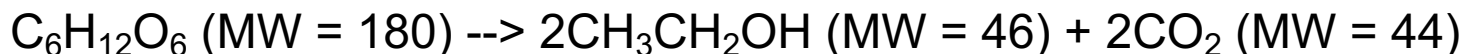
## Target: Liquid Hydrocarbons, fuel of the past ... and future

- Unbeatable Energy vs. weight ratio
- “Nature’s choice” across the tree of (mobile) life

### Petroleum vs. Biomass: *U.S. is C limited*



## Today's biofuels from fermentation: Ethanol (butanol, etc.):



Process concentrates low **E** of sugars into half the mass, **but loses 1/3 of the C**  
Ethanol is not close to a 1:1 gasoline or diesel replacement

## NJ Bias:

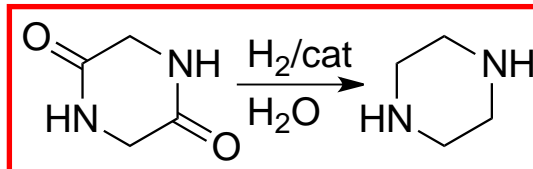
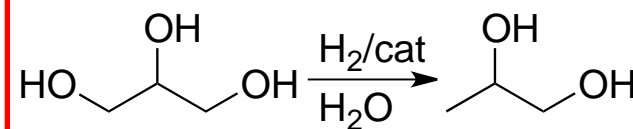
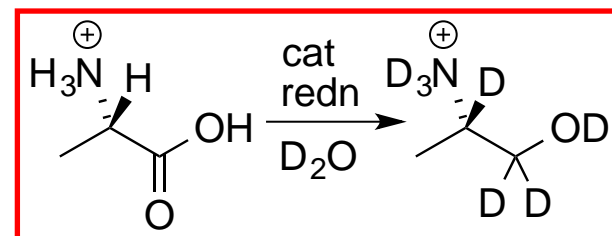
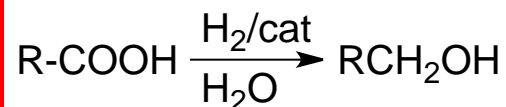
*Electroreductive “energy upgrading” of plant-derived Carbon is critically needed to maximize its utilization*

- At base, biomass-to-energy strategies are **solar energy capture schemes**
- Making practical liquid fuels (i.e. hydrocarbons) renewably also requires a scheme for **carbon capture and retention**
- Compare plant and human technologies:
  - **Energy:** **Plants** are poor (ca. **1% efficient**) at capturing solar energy and storing it in chemical form. But today's commercial **PV** and other solar E capture methods routinely **exceed 10%**--an order of magnitude!  
Problem: These technologies mainly produce their energy as **electrical power**.
  - **Carbon:** Plants are champions at capturing the very dilute CO<sub>2</sub> from the atmosphere. No serious human technology comes close...
- *1. Let plants do what they do best--capture C from a very dilute supply*
- *2. Let humans do what we do better--capture E from plentiful sunlight*
- *3. Develop the biology/chemistry to combine 1+2, to maximize utilization of biomass carbon by raising its energy content*
- Simple, general, low cost processing steps will be essential

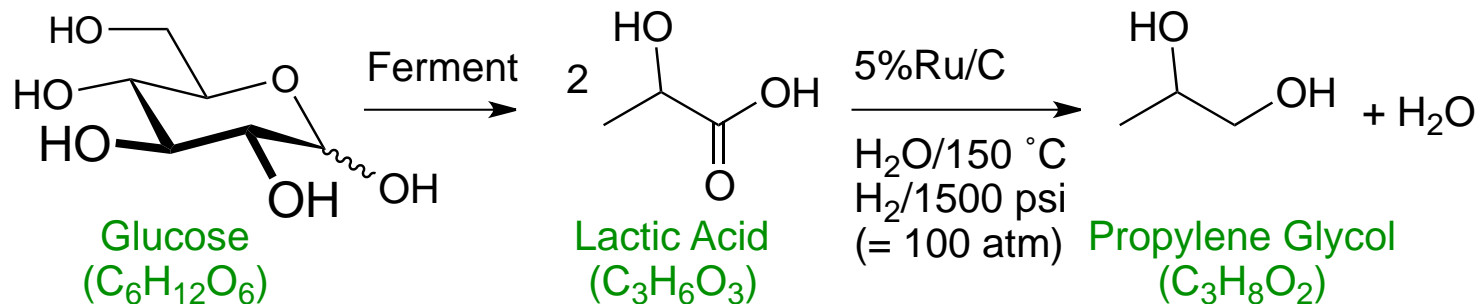
## **Background: bio-based building blocks at MSU**

A 20+ year collaboration of JEJ's and Dennis Miller's groups, focused mostly on commodity and fine chemicals

- Hydrogenation of carboxylic acids
- Electroreductions/electrohydrogenations
- Comparing of electro- vs. classical catalytic hydrogenations
- Electrocatalytic C-H activation
- Hydrogenolysis of glycerol + polyols)
- Polyol separations/reactive distillation
- Hydrogenation of amides to amines



## Lactic Acid: the “other” glucose fermentation product as a biomass-based feedstock



### Ideal “green” substrate--must be in $\text{H}_2\text{O}$ :

- $-\text{COOH} + -\text{OH}$  groups form esters

### Carbon-retentive fermentation:

- Yields exceed 0.95 lb/lb glucose

### Lactic and Propanoic Acid:

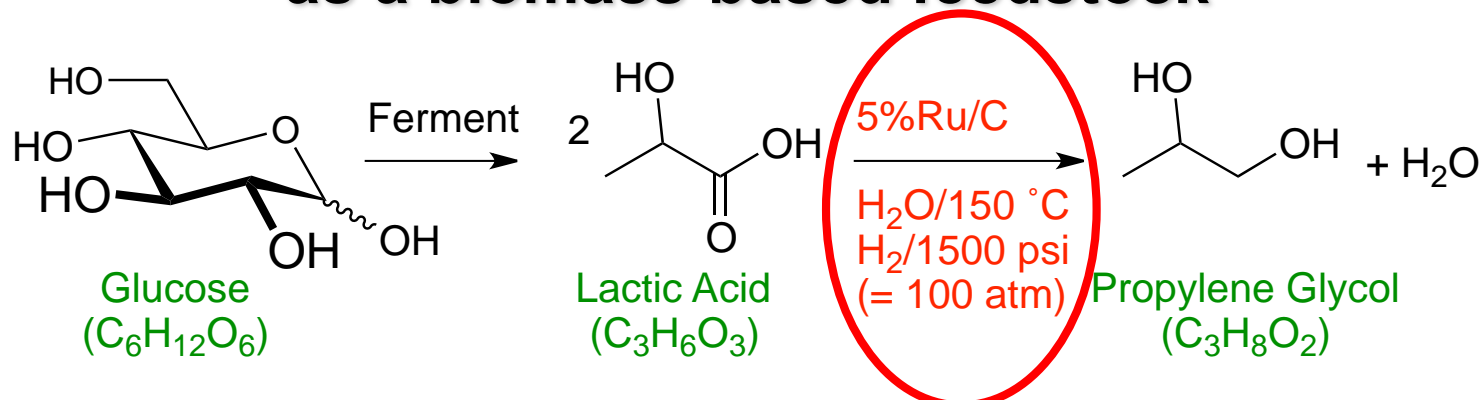
**Kinetics:** with Y. Chen, D. J. Miller, *Ind. Eng. Chem. Res.* **2007**, 46, 3334-3340.

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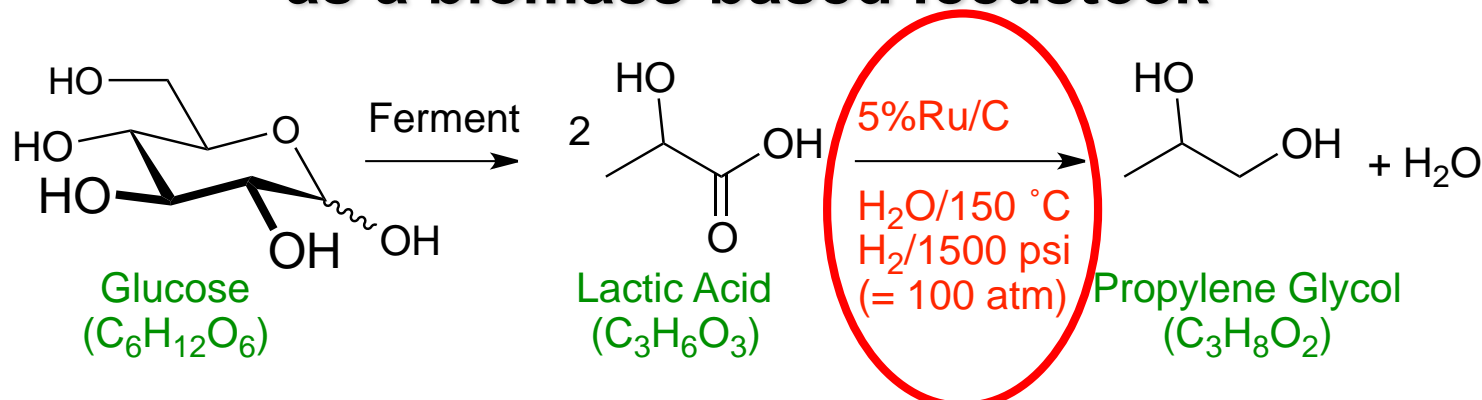
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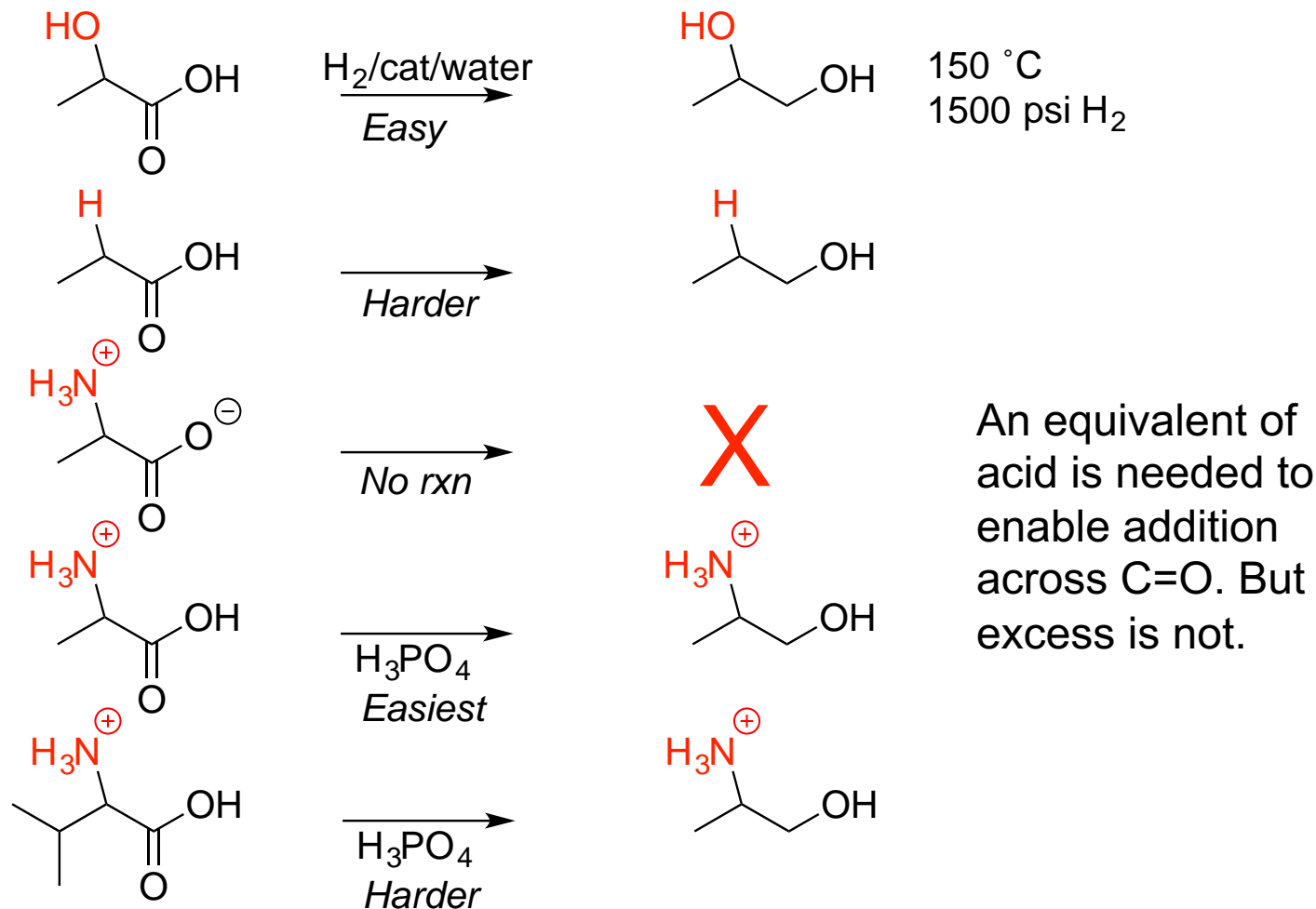
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**Poor  $H_2$  solubility in  $H_2O$ !**

**Make H atoms needed at Ru catalyst surface by electro-chemical reduction of  $H^+$ !**

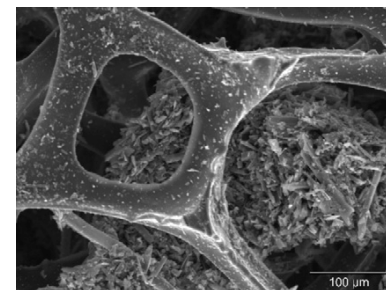
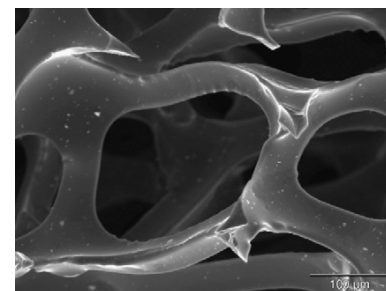


## Lessons from classical hydrogenation studies at MSU:



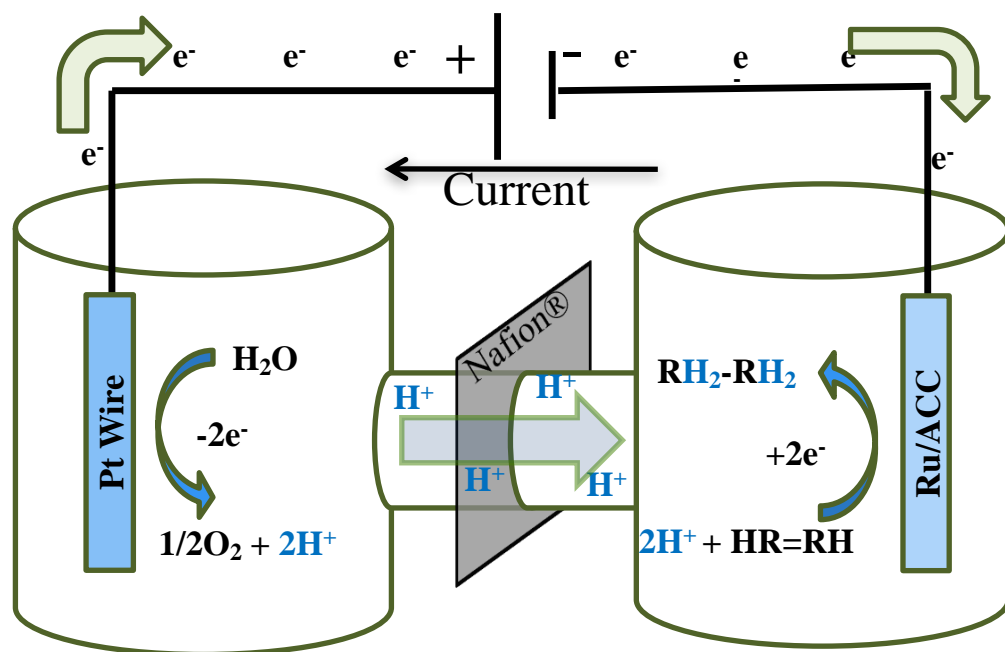
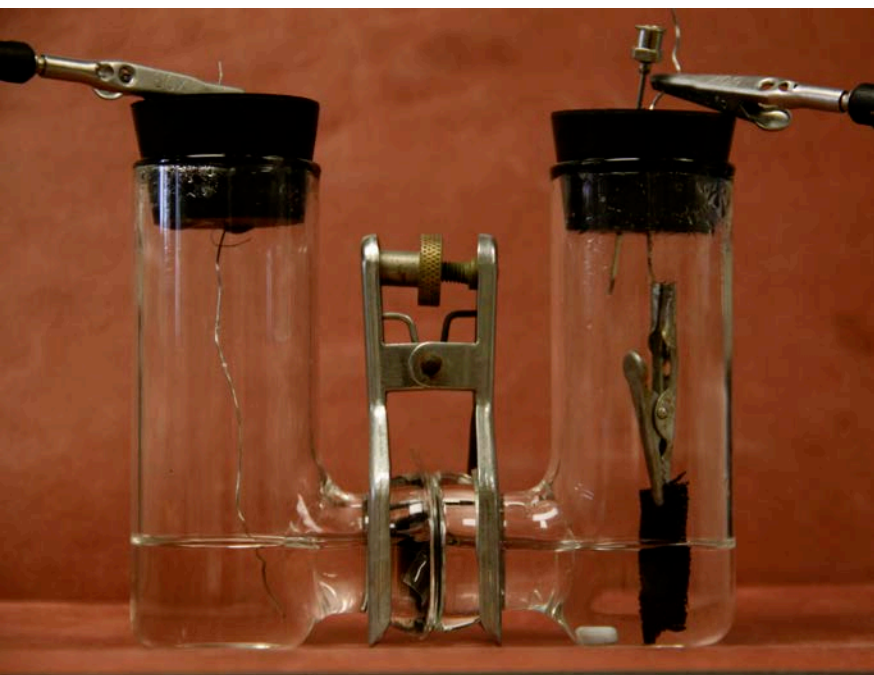
# Electrocatalytic hydrogenation (ECH)?:

- Problem: Low  $\text{H}_2$  solubility in  $\text{H}_2\text{O}$   $\longrightarrow$  high pressures (1500 psi, 150 °C)
- What about forming the  $\text{H}_2$  at an electrode of catalytic metal?
- Enables mild hydrogenation of difficult substrates ( $P = 1 \text{ atm}$ ,  $T < 100 \text{ }^\circ\text{C}$ ), with the same catalyst (in RVC), but... no  $\text{H}_2$  and no high pressure gas handling/storage.
- Safer process, cheaper equipment, uses less energy.
- Method enables in situ spectroscopic studies for mechanistic analysis under mild conditions.
- Solvent studies show  $\text{H}_2\text{O}$  is best solvent for ECH
- ECH of other substrates (aromatics) now underway

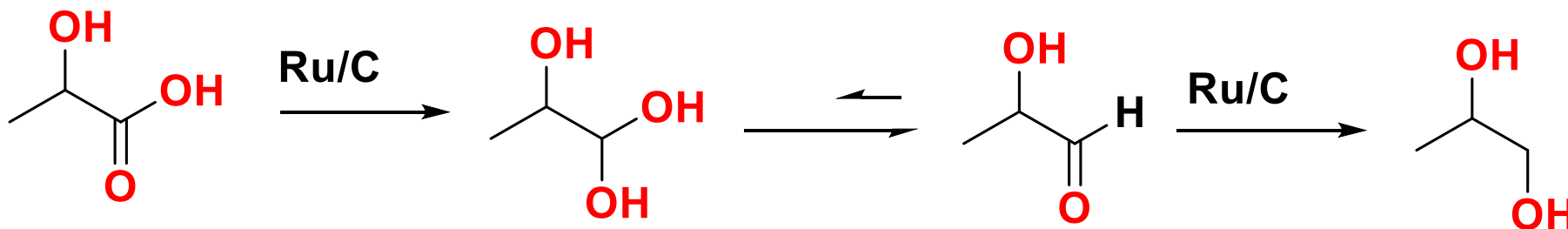


“Mild electrocatalytic hydrogenation of lactic acid to lactaldehyde and propylene glycol” with **T. S. Dalavoy**, G. M. Swain, D. J. Miller, J. Li, and J. Lipkowski, *J. J. Catal.* **2007**, 246, 15-28.

# Electrocatalytic Hydrogenation and Deoxygenation

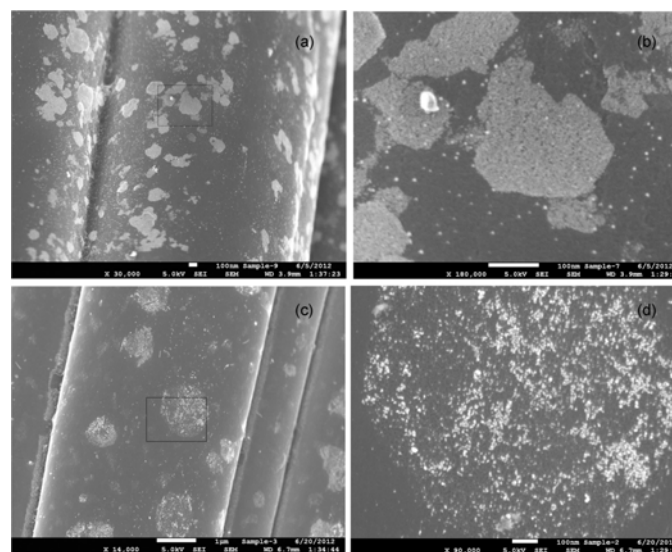
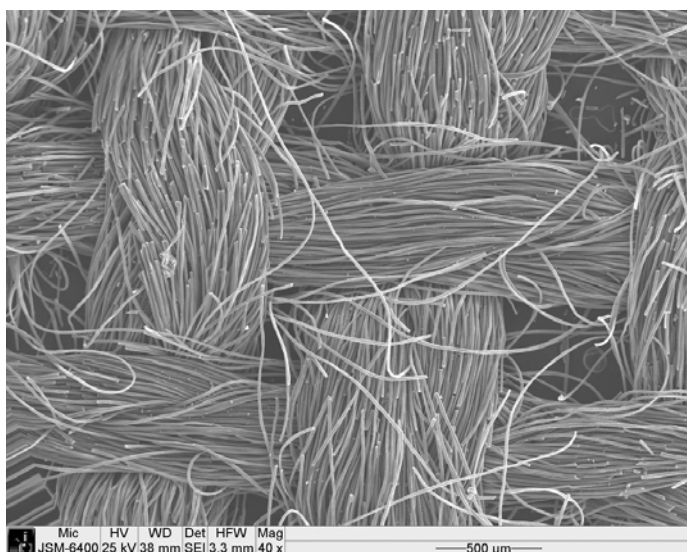


# ECH of lactic acid with Ru/C catalyst



T.S. Dalavoy (MSU) *Journal of Catalysis* **2007**, 246, 15–28

Ru-impregnated Carbon cloth electrodes

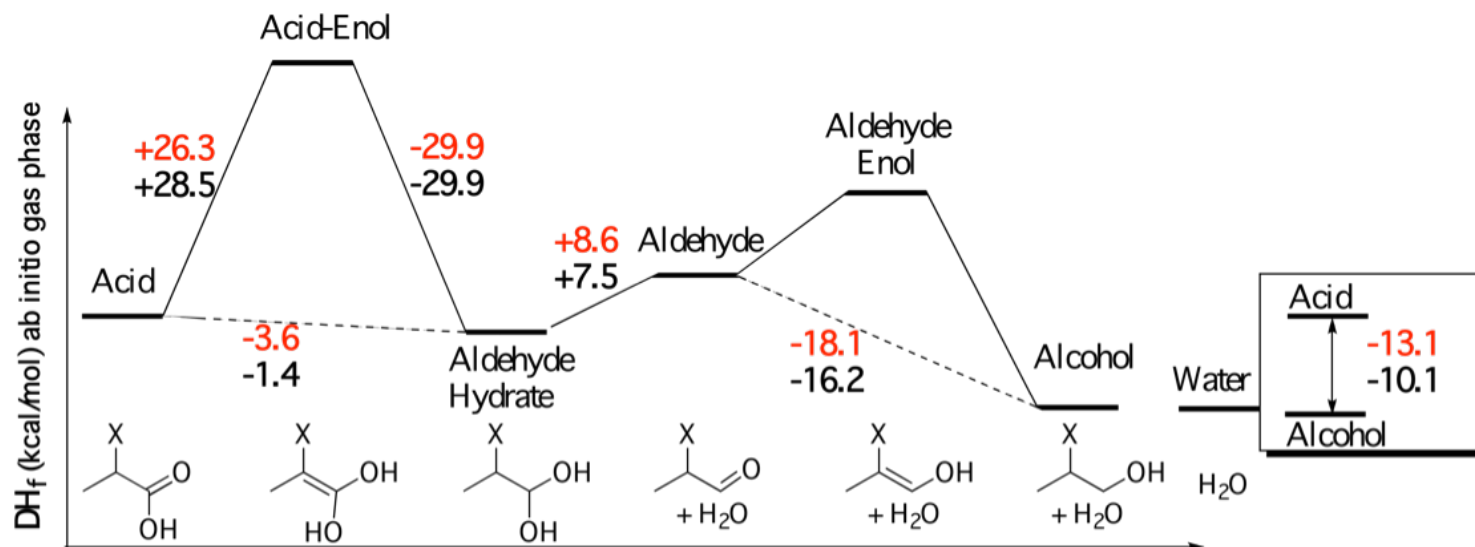


Li, Zhenglong (MSU) *Green Chem.*, **2012**, 14, 2540

80%  
20 h

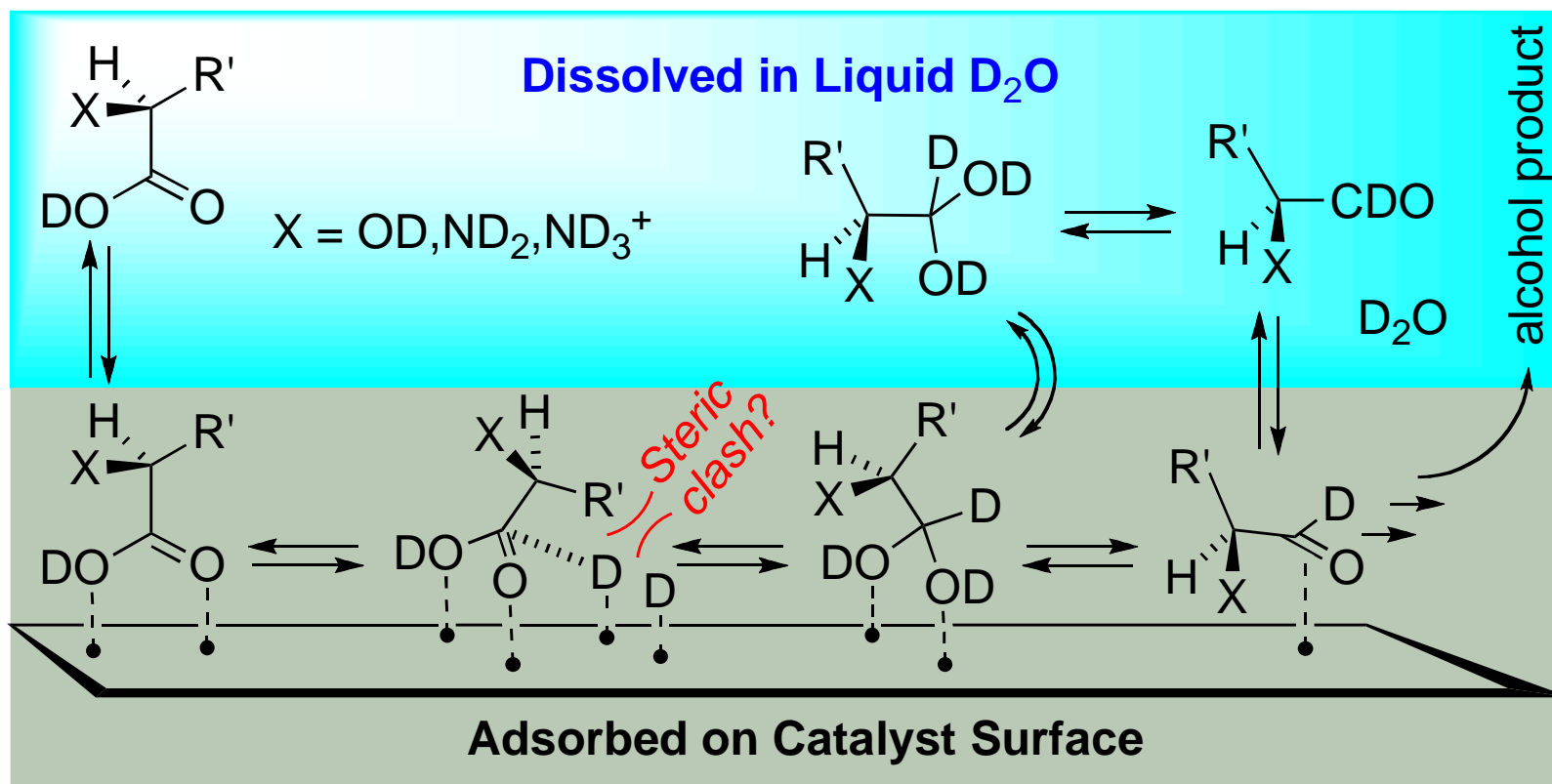
# Ab Initio G3 “gas phase” and “solvated” Energetics

Is LA just more exothermic? Only a little...



LA: (X=OH) kcal/mol	G 3, gas	-147.9	-121.5	-151.5	-85.3	-79.2	-103.4	-57.6	-13.1
	G 3, aq.	-158.8	-133.7	-163.5	-92.6	-87.4	-113.3	-64.0	-18.5
	Exp., gas	-	-	-	-	-	-102.7	-57.8	-
	Exp., aq.	-161.4	-	-	-	-	-119.7	-68.3	-26.6
PA: (X=H)	G 3, gas	-108.9	-80.4	-110.3	-45.2	-35.5(cis)	-61.4	-57.6	-10.1
	G 3, aq.	-116.0	-90.2	-119.7	-49.1	-41.8	-66.2	-64.0	-14.2
	Exp., gas	-109.0	-	-	-45.1	-	-61.1	-57.8	-9.9
	Exp., aq.	-122.1	-	-	-52.2	-	-72.3	-68.3	-18.5

# Proposed mechanism of -COOH reduction



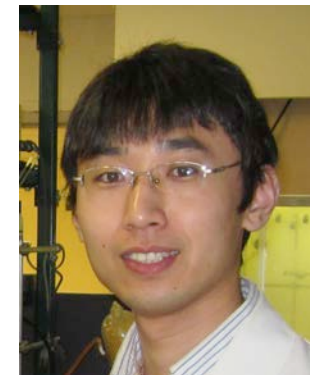
**Kinetics:** -COOH binding similar for all acids; bigger R' -> slower reduction.

**Spectroscopy:** -COOH binds head-on.

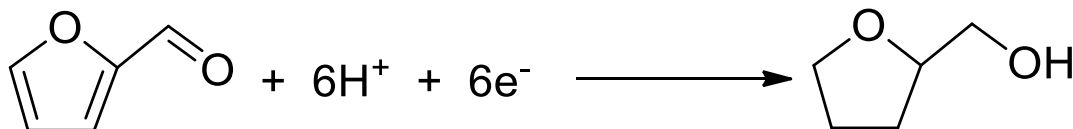
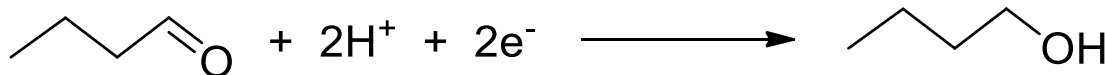
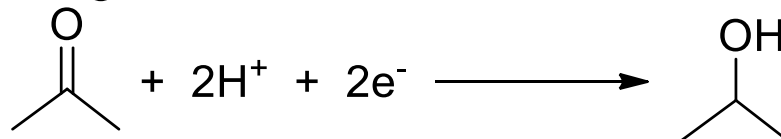
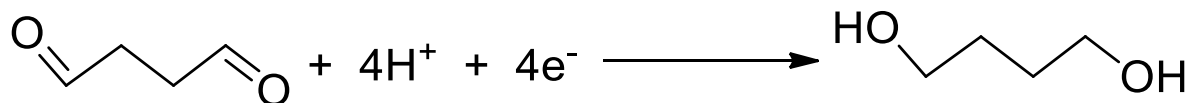
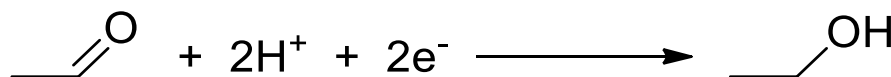
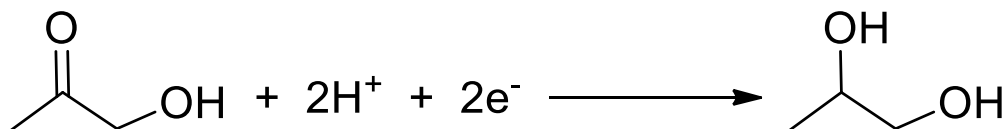
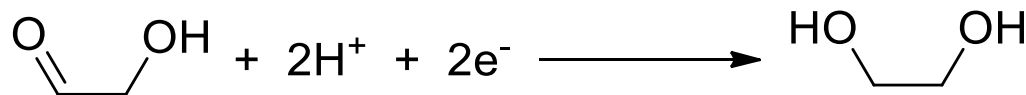
**Mechanism:** Bonding to H requires bending over at the COOH carbon.

# ECH of Water-soluble Bio-oil:

Carbonyl reductions—easy, but even here,  
current efficiency is rarely ideal



Dr. Zhenglong Li

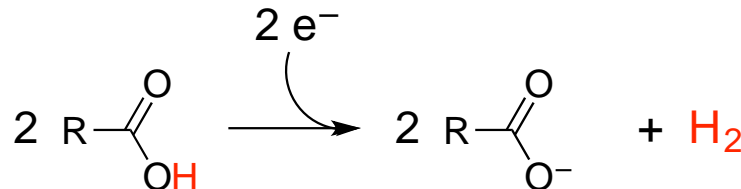


**Carbonyl conc.:** 0.2 mol/Kg (Initial)  $\rightarrow$  ~0 mol/Kg (6.5 hr)

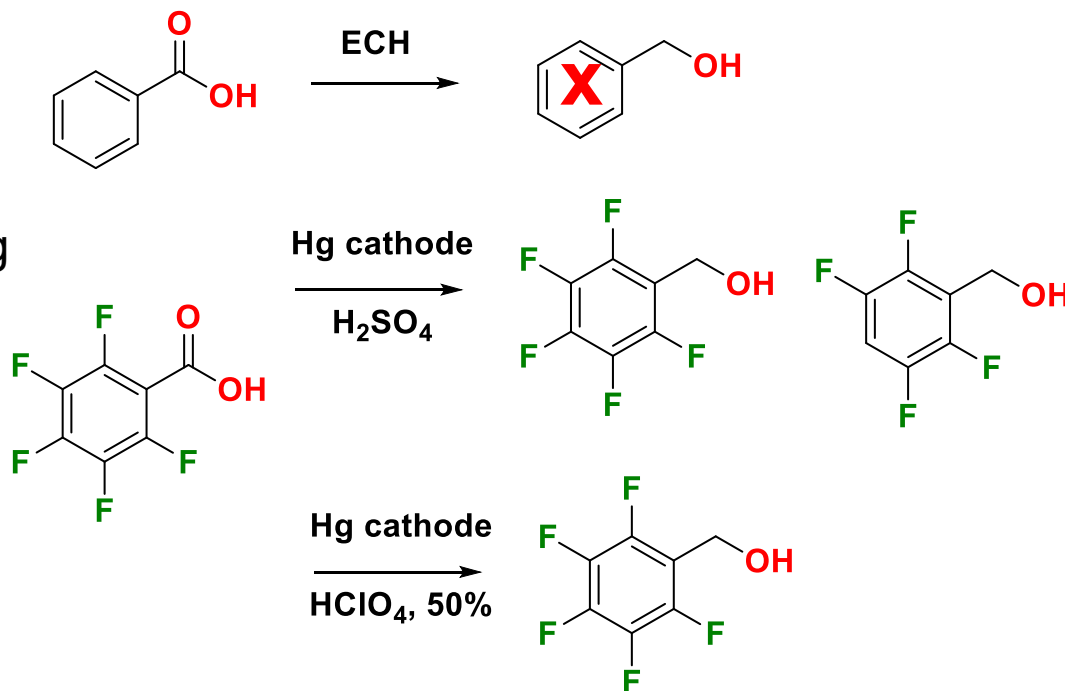
...with Li Z., *et al*; *Green Chem.* **2014**, *16*, 844-852.

# ECH of carboxylic acids: The challenge...

Challenge 1: Acid favors  $H_2$  formation under ECH conditions, and carboxylate anion resists reduction, so current efficiency is low to 0



Challenge 2: Aliphatic acids are unreactive; usually need activation by electron withdrawing groups for reduction to compete with  $H_2$  evolution.





## **ECH of free carboxylic acids: The challenges...**

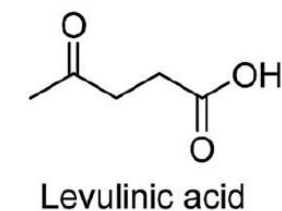
Challenge 3: Reduction of protons shifts electrolyte pH. Classically cited examples of butanoic or phenylacetic acid reduction thus typically were performed in brutal and costly media such as 50% sulfuric acid, and in only modest yields.

**Reduction of esters works reasonably well, but except for triglycerides, this still typically requires strong acids and is not very relevant to biomass conversions. Substantial work has looked at hydrogenation of unsaturated vegetable oils, mostly in organic solvents.**

**Similarly, aldoses are widely reduced to sugar alcohols, but free sugars seem non-relevant to AD.**

# Levulinic Acid reactions

Pb electrode:  
Reductions  
studied by Tafel  
himself.

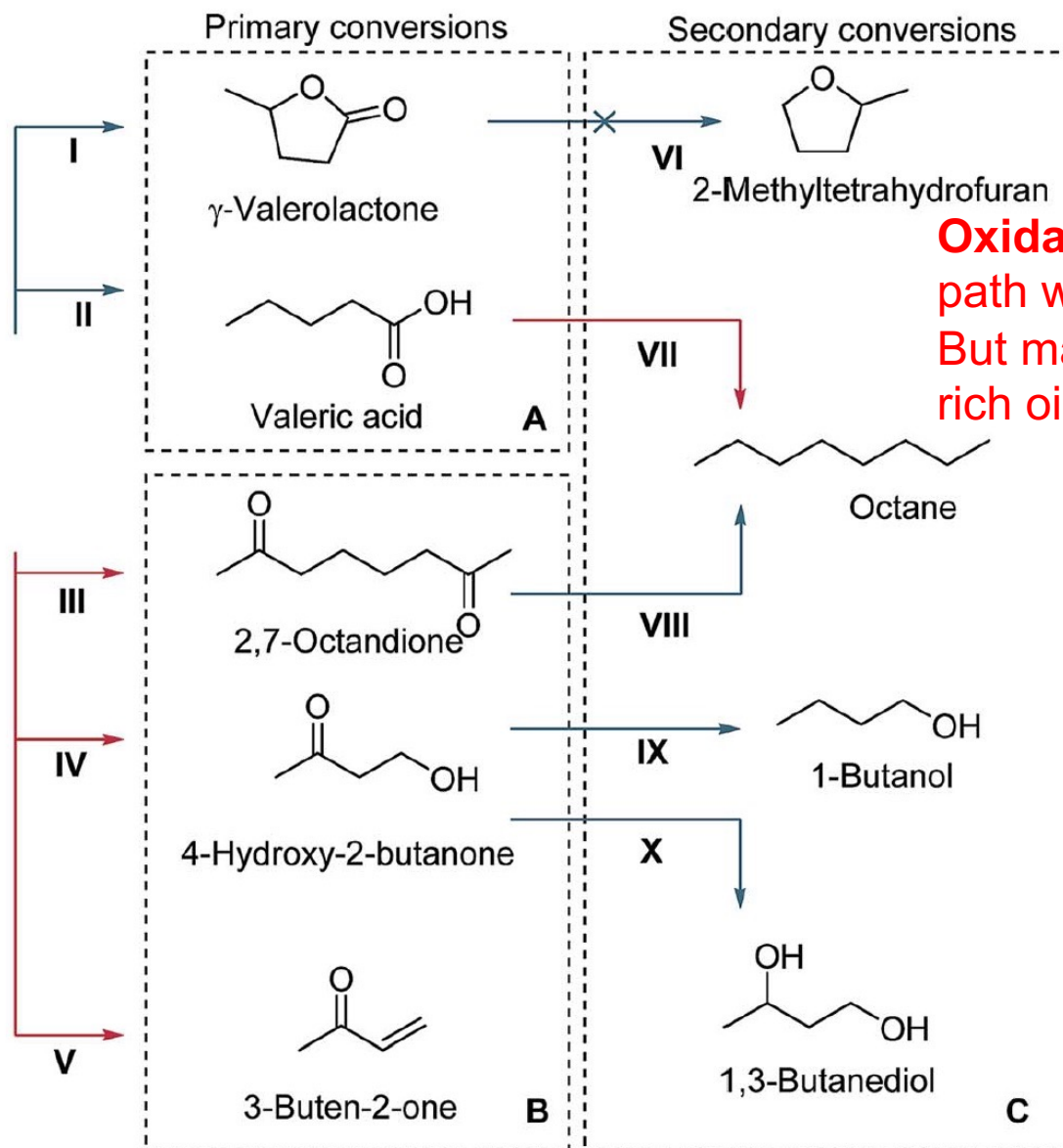


reduction

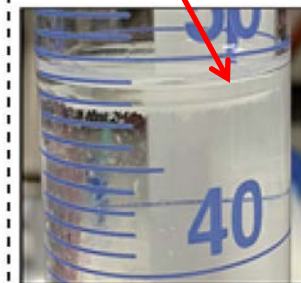
oxidation

Notably missing:  
RCO<sub>2</sub>H reduction

Figure from  
Schröder *et al.*



**Oxidative** Kolbe rxn  
path wastes Carbon  
But makes alkane-  
rich oily layer



# Levulinic Acid: Opportunity or just another ketone?

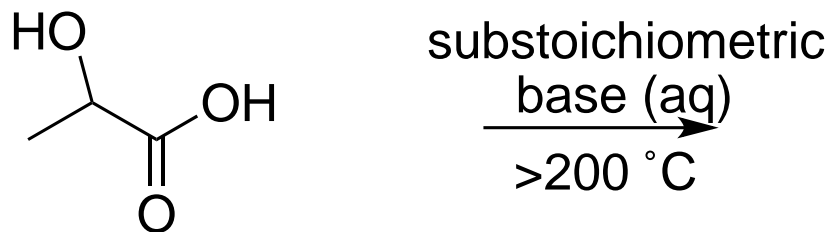
“The results suggest that the proposed integrated electrocatalytic biorefinery process, though very promising, currently remains challenging. Advanced electrocatalytic materials that can tolerate impurities existing in the streams of a crude biomass process need to be developed....”

Wenzhen Li *et al.*, “Integrated electrocatalytic processing of levulinic acid and formic acid to produce biofuel intermediate valeric acid” *Green Chem.*, **2014**, 16, 1305.

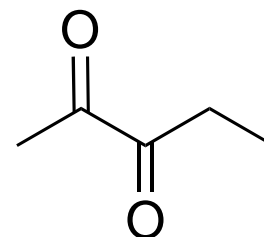
Wenzhen Li *et al.*, “Electricity Storage in Biofuels: Selective Electrocatalytic Reduction of Levulinic Acid to Valeric Acid or gamma-Valerolactone” *ChemSusChem*, **2013**, 6, 674.

Uwe Schröder *et al.*, “Electrochemistry for the generation of renewable chemicals: electrochemical conversion of levulinic acid” *RSC Advances*, **2015**, 5, 26634.

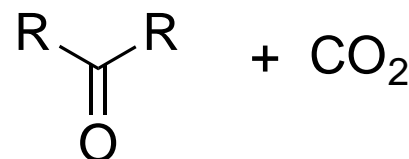
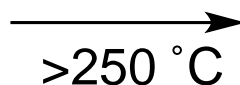
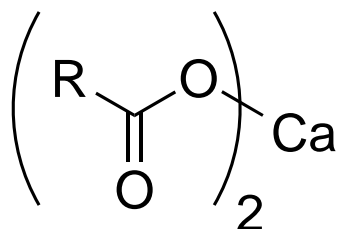
Two additional paths from carboxylic acids to more hydrophobic/fuel-like potentially high-value ketones



Lactic acid



2,3-pentanedione  
= microwave popcorn odor

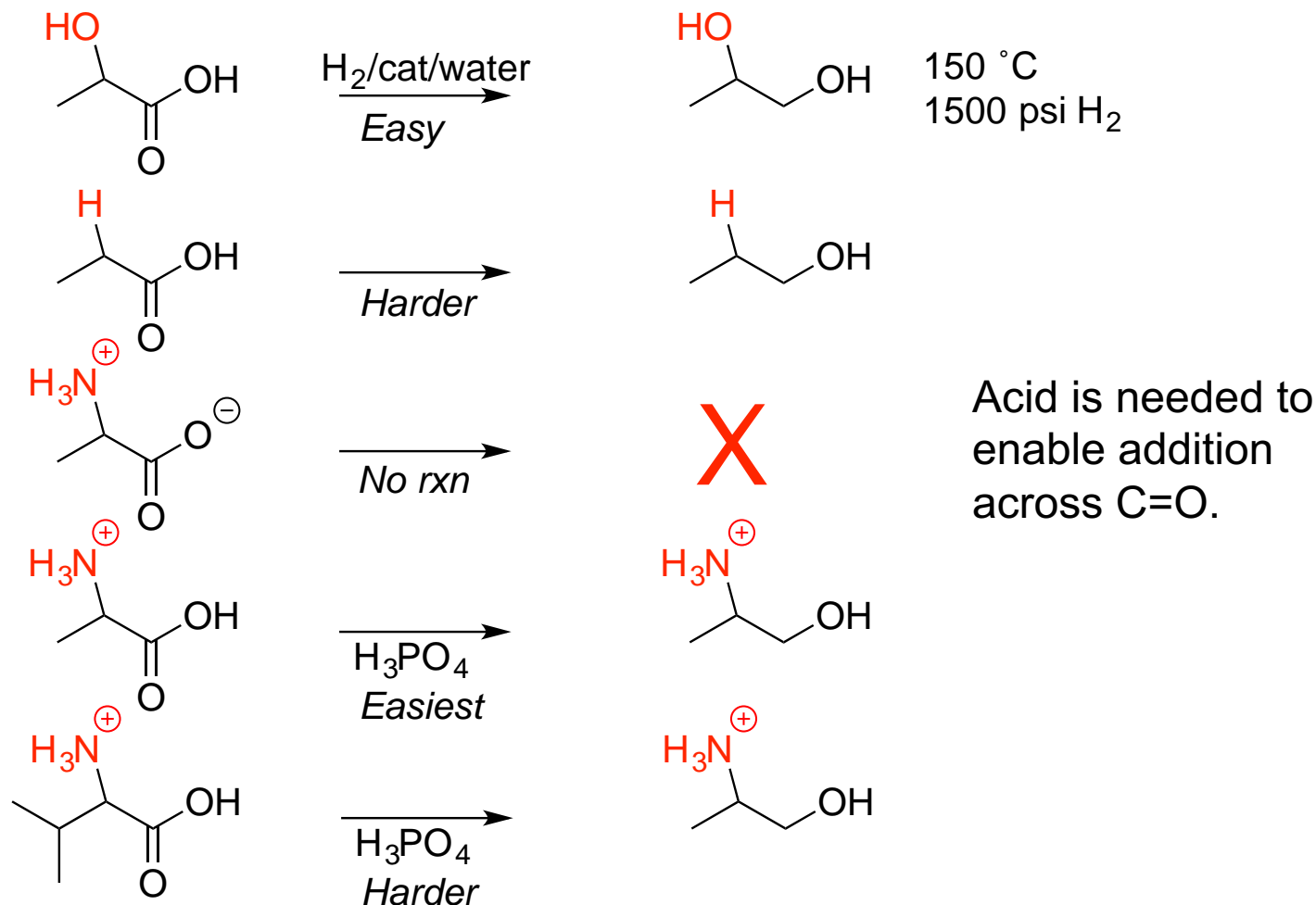


R = C3 to C8 alkyl; dicarboxylic acids also give cyclic ketones

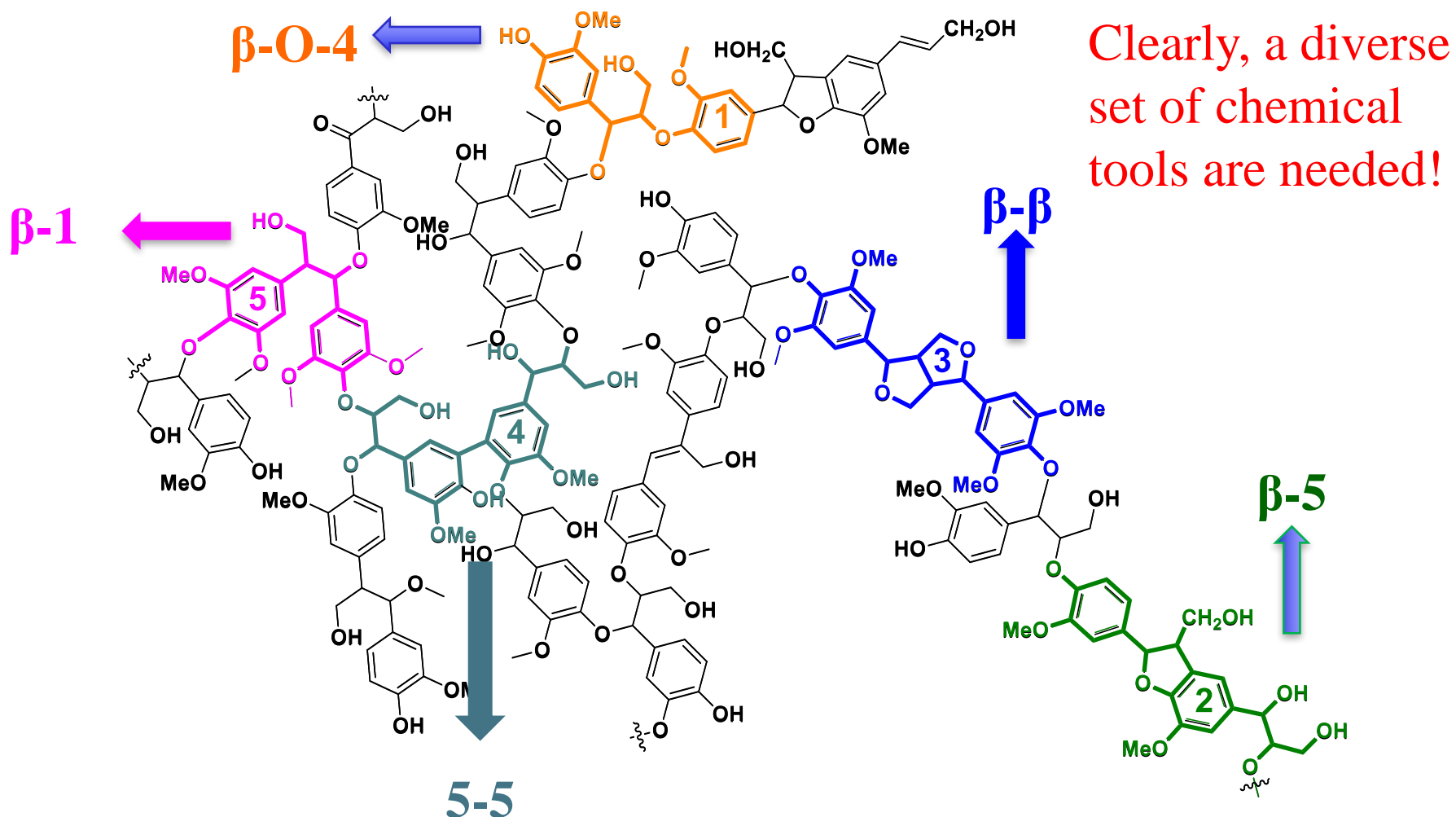
Gunter, G. C.; Langford, R. H.; Jackson, J. E.; Miller, D. J. "Catalysts and Supports for Conversion of Lactic Acid to Acrylic Acid and 2,3-Pentanedione" *Ind. Eng. Chem. Res.* **1995**, 34, 974-980.

Murkute, A. D.; Jackson, J. E.; Miller, D. J. "Supported Mesoporous Solid Base Catalysts for Condensation of Carboxylic Acids" *J. Catal.* **2011**, 278, 189-199.

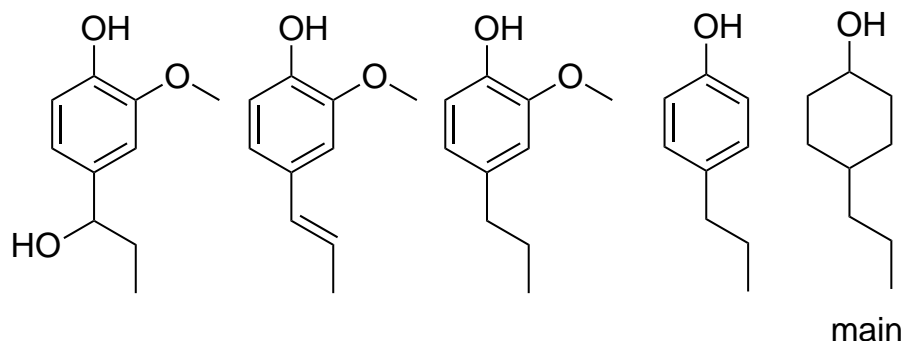
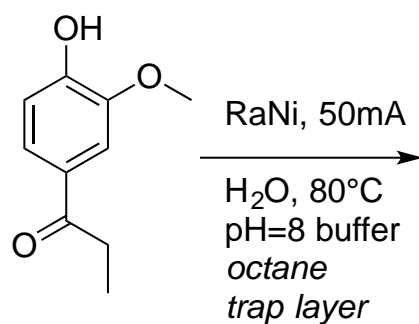
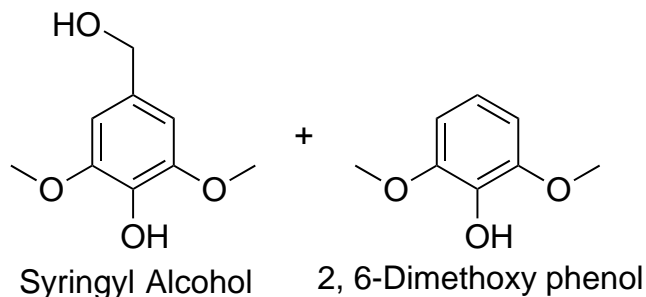
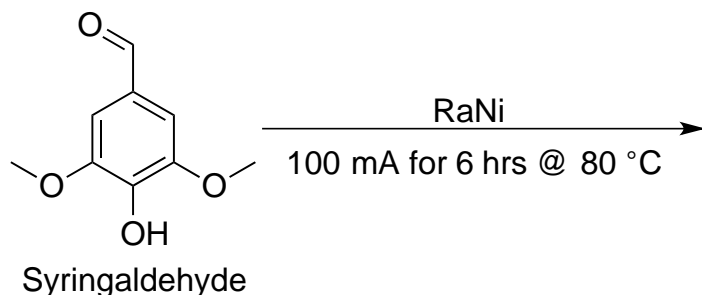
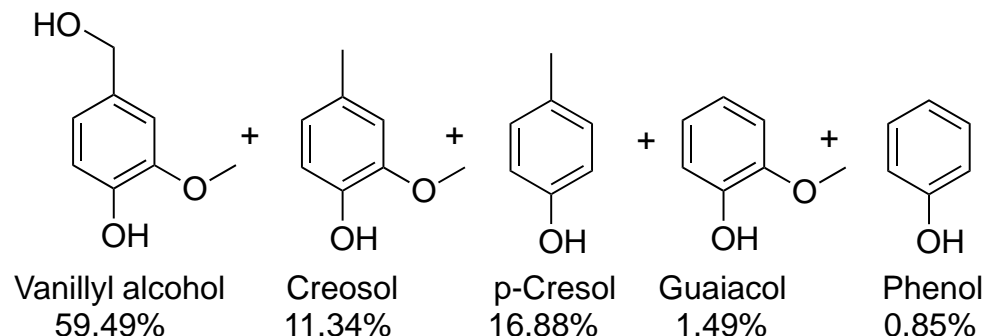
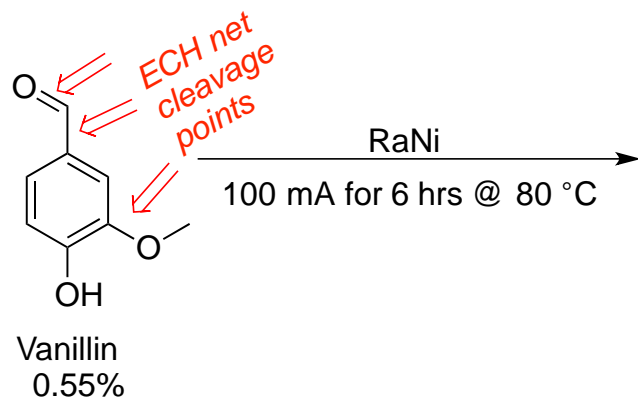
Opportunity—it seems as if we're so close...  
The right catalyst may still be just around the corner:



# A different opportunity: carbon-rich, underutilized lignin residues



# Raney Nickel electrocatalytic deoxygenations



**Reduction and deoxygenation:**  
 Hydrophobic cpds extracted into an overlying octane layer

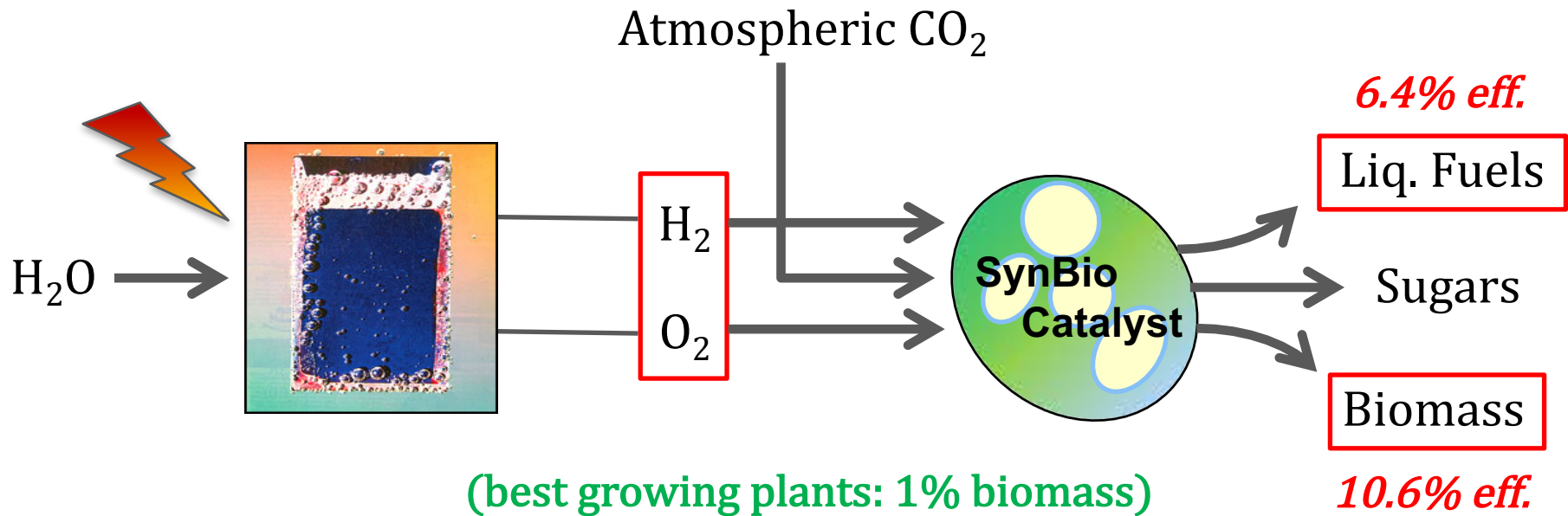
## Random final thoughts: Scale and separations?

- What about scale? Chlor-alkali is practiced on a scale of 500 million ton/year; large industrial reactors have been known for years. Acrylonitrile dimerization to adiponitrile has been industrially implemented in nylon production.
- Could electrochemistry be used to acidify to enable acid neutralization/extraction into organic phases?
- How about electroprecipitation of, say, phosphates?
- Sulfide/thiol electrochemistry for odor control has been demonstrated; R-SH/RSSR interconversion are also well known electrochemical processes.



# Emerging Competition: Nocera and Silver's "Artificial Leaf"

## Hydrogen to Liquid Fuels



Science **2016**, 352, 1210. Slide kindly shared by D. G. Nocera.

## **ECH advantages and recent advances**

- Simplicity: mild temperature, ambient pressure conditions
- Low-cost metal electrocatalysts key
- Lifetime or reactivation/recycle (up to 10x so far with Raney Ni)
- Aryl ether cleavage under mild conditions
- Hydrocarbon trap layer enhances reduced (fuel-like) product recovery
- Dealkylation/deacylation of aryl rings via carbon-carbon cleavage
- Mechanistic insights into surface C-O cleavage process, activating interactions between aromatic substrates
- Diffusible redox mediators, continuous flow reactors in development
- Many undergrads involved and excited