

Biomass Deconstruction, Conversion, and Upgrading to Fuels

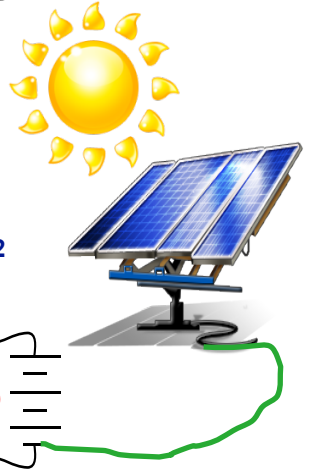
Biomass



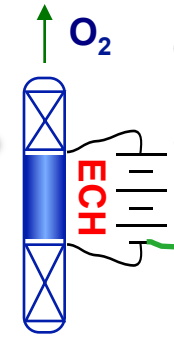
Pretreatments

AHP/enzyme
AFEX
E-AFEX

Chemical conversion



Chemically Tractable Biomass carbon
(polyols, aromatics)



Liquefaction
Pyrolysis

Energy Upgrading
ECH, hydrotreating

**Liquid Fuels
Chemicals**

Participating Research Groups and Interests

Jonathan Walton (Plant Biology and PRL)

- MSU director GLBRC
- Enzymatic and chemical biomass pretreatment for sugar release

Bruce Dale (Chemical Engineering and Materials Science)

- AFEX™ biomass pretreatment and activation
- Life cycle & supply chain economic analysis

Chris Saffron (Forestry + Biosystems, Chem., & Ag. Engg.)

- Thermal biomass processing, especially fast pyrolysis
- Supply chain economics

Ned Jackson (Chemistry)

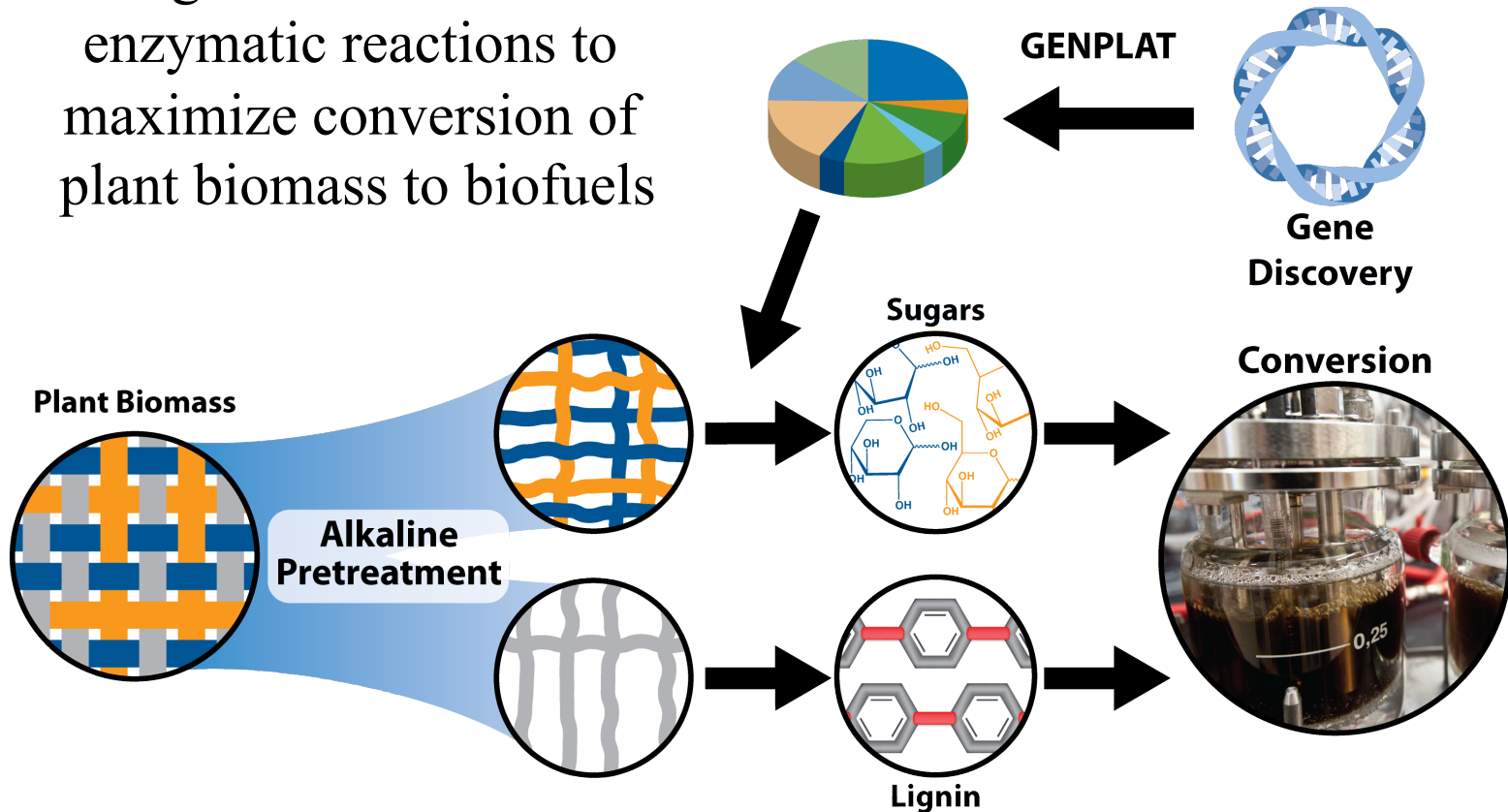
- Catalysis and electrocatalysis
- Organic reaction mechanisms

Dennis Miller (Chemical Engineering and Materials Science)

- Catalytic hydrogenation and reactor design
- Process economics

GLBRC: Overview of Deconstruction Research

Integrate chemical and enzymatic reactions to maximize conversion of plant biomass to biofuels



GLBRC: Biofuel Production Flowchart: Sugar Platform

Cellulose Process

Corn Process

Sugar Cane Process

DALE LAB WORKS HERE- AFEX PROCESS

Cellulose

Cellulose Pretreatment

Cellulose Conversion Hydrolysis

Corn Kernels

Starch Conversion (Cook or Enzymatic Hydrolysis)

Sugar Cane

Sugar

Fermentation

Distillation

Drying

Biofuels

Co-Product Recovery
Animal Feed
Chemicals

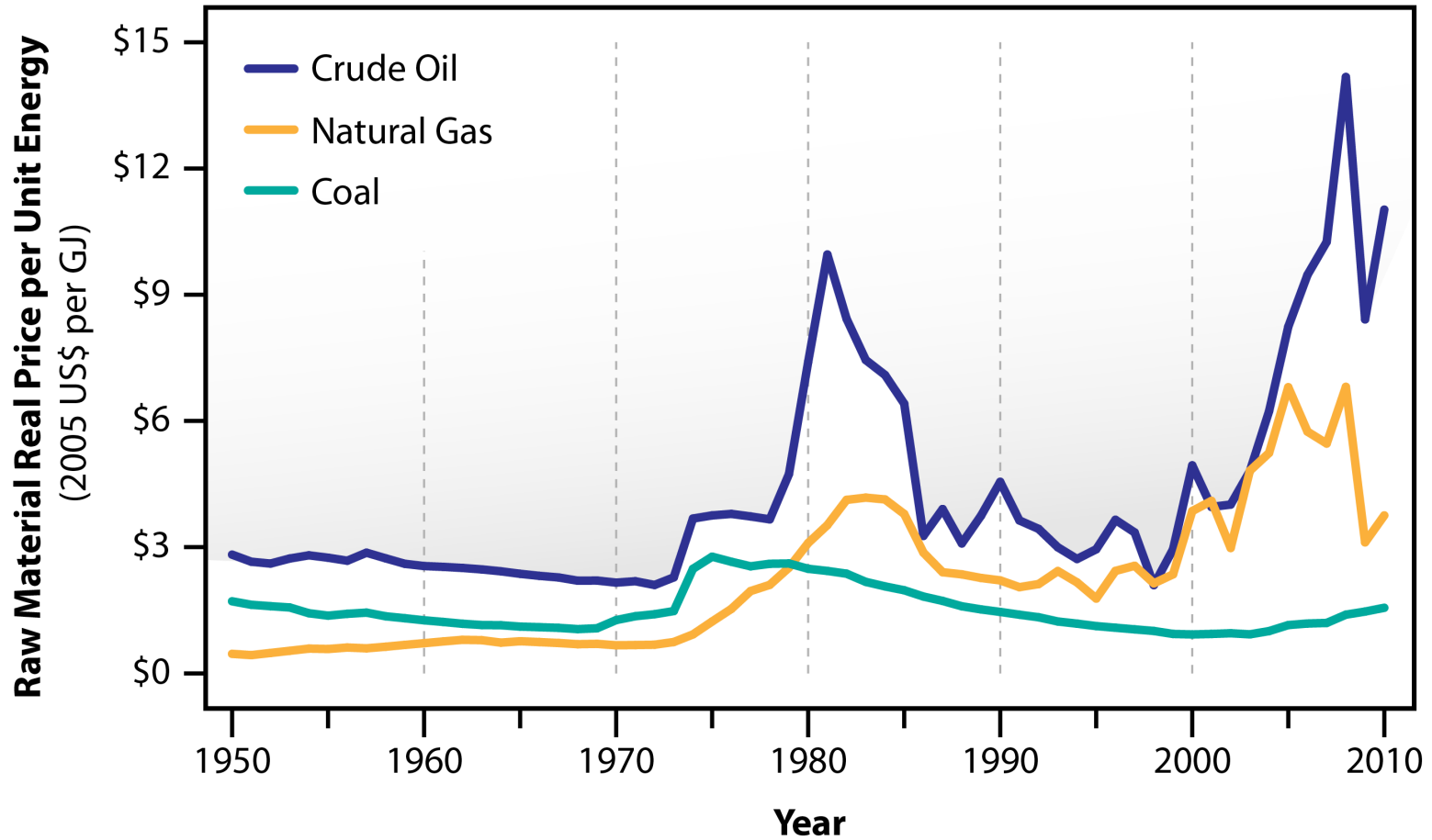
- Corn Stover
- Grasses
- MSW
- Forest Residues
- Ag Residues
- Wood Chips

Objective is to generate clean, fermentable sugars @ about **15¢ per pound**

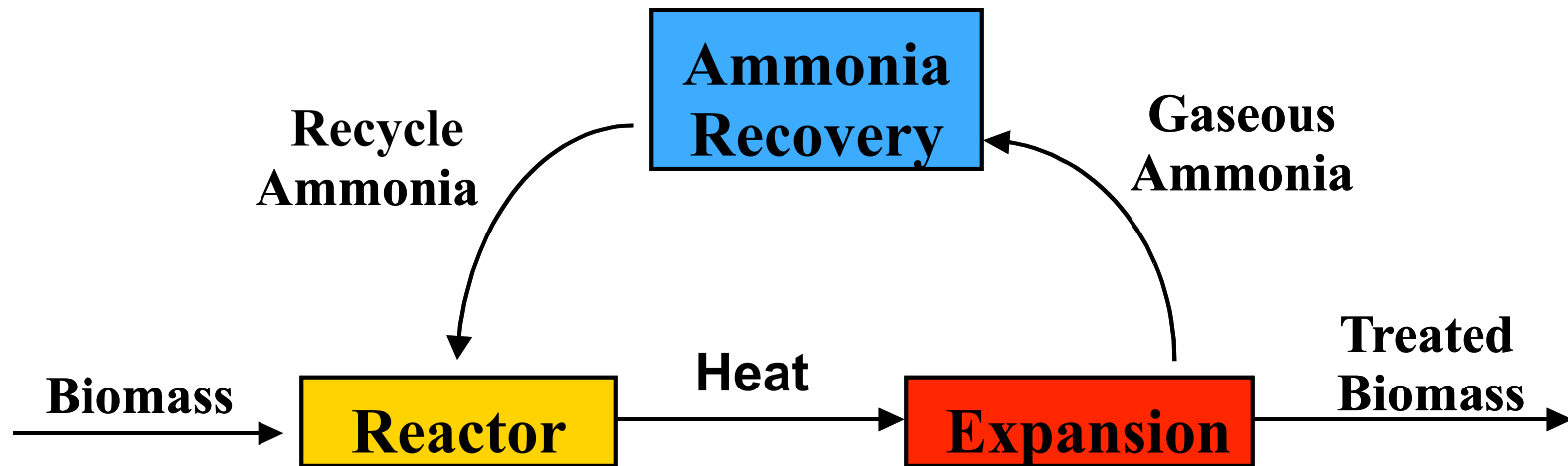
Some Basic Energy Facts

- **Services** we need from energy (current primary sources of these services)
 - **Heat** (natural gas, coal)
 - **Light/electricity** (coal, natural gas, hydro/nuclear)
 - **Mobility** (oil—96%, ethanol, CNG)- *powers most commerce*
- **All energy services (all BTU, ergs, GJ) are not created equal—we value mobility (=oil) above all other energy carriers**
- Electricity/batteries can never provide more than about half of mobility needs—and they cannot support commerce at all
- Commerce moves by trucks, ocean shipping, rail & jet aircraft
- Economic chaos results when liquid fuel demand exceeds supply
- *Liquid fuels: not “energy” is the key economic security issue—and right now liquid fuels means refined oil products*

Comparative Value of U.S. Energy Sources over Time



AFEX™ Process Overview

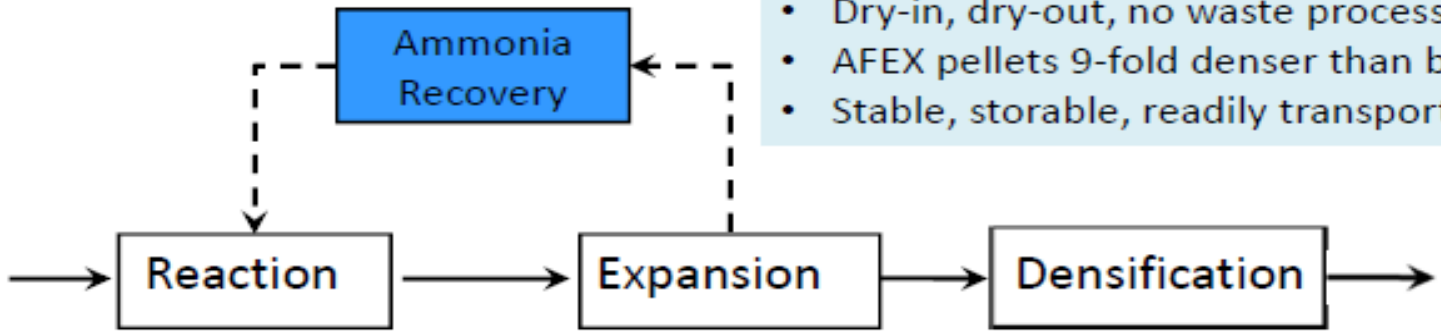


AFEX™ process description and properties

- Hot (~100 C), concentrated (~15M) ammonia:water mix, short reaction time
- rapid pressure release ends treatment, cools system,
- little biomass degradation, high sugar yields, residual nitrogen has value
- no separate liquid phase (“dry to dry”), low water use, sterile product
- high solids loadings possible by fed batch fermentation (eg, ~ 40% solids)
- no loss of nutrients (eg, from corn stover) in wash stream
- highly fermentable material after AFEX treatment without further processing
- very effective on all grasses and residues we have tested, not great on hardwoods (needs higher T & ammonia loadings), ineffective on softwoods

AFEX™ Biomass Pretreatment

- Applicable to variety of ag residues
- Dry-in, dry-out, no waste process
- AFEX pellets 9-fold denser than biomass
- Stable, storable, readily transportable



Raw Biomass



Treated Biomass

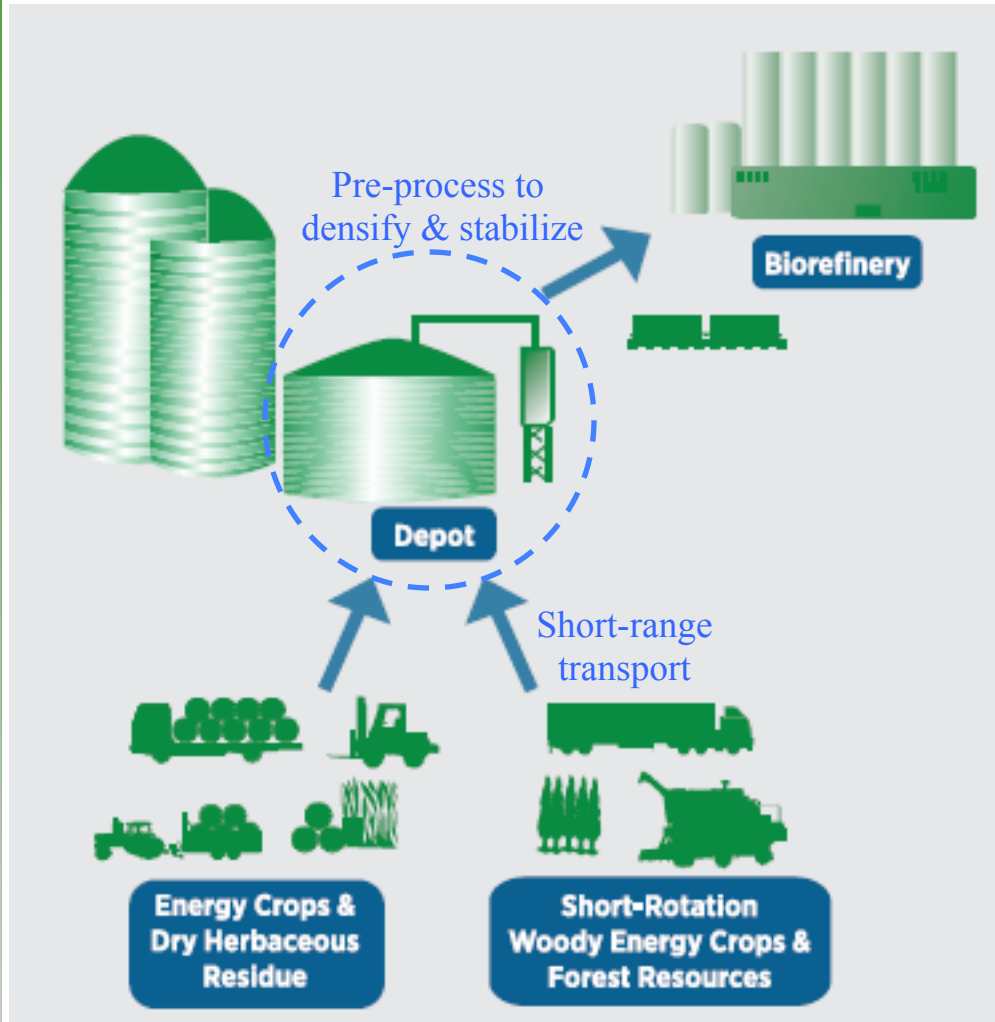


AFEX Pellets

Importance of Low-Tech, Locally Implemented Tools Regional Biomass Processing Depots (RBPDs)

- Large scale biofuels will require moving huge quantities of bulky, low density biomass—moving mostly “thin air”
- This is simply not tenable... therefore we must densify the energy content of the biomass close to where it is grown
- Provides opportunities for advancing rural economies by adding value to the biomass near the farm or forest
 - More jobs in rural areas
 - More wealth creation in rural areas
 - Produce energy products in rural areas
- Requires low capital investment technologies

Regional Biomass Processing Depots (RBPDs)



The Challenge of Biomass:

- Dispersed distribution
- Low bulk density
- Low specific energy

Depot Concept:

Local depots would act as collection and pre-processing points for diverse biomass resources to ensure feedstock compatibility with downstream infrastructure

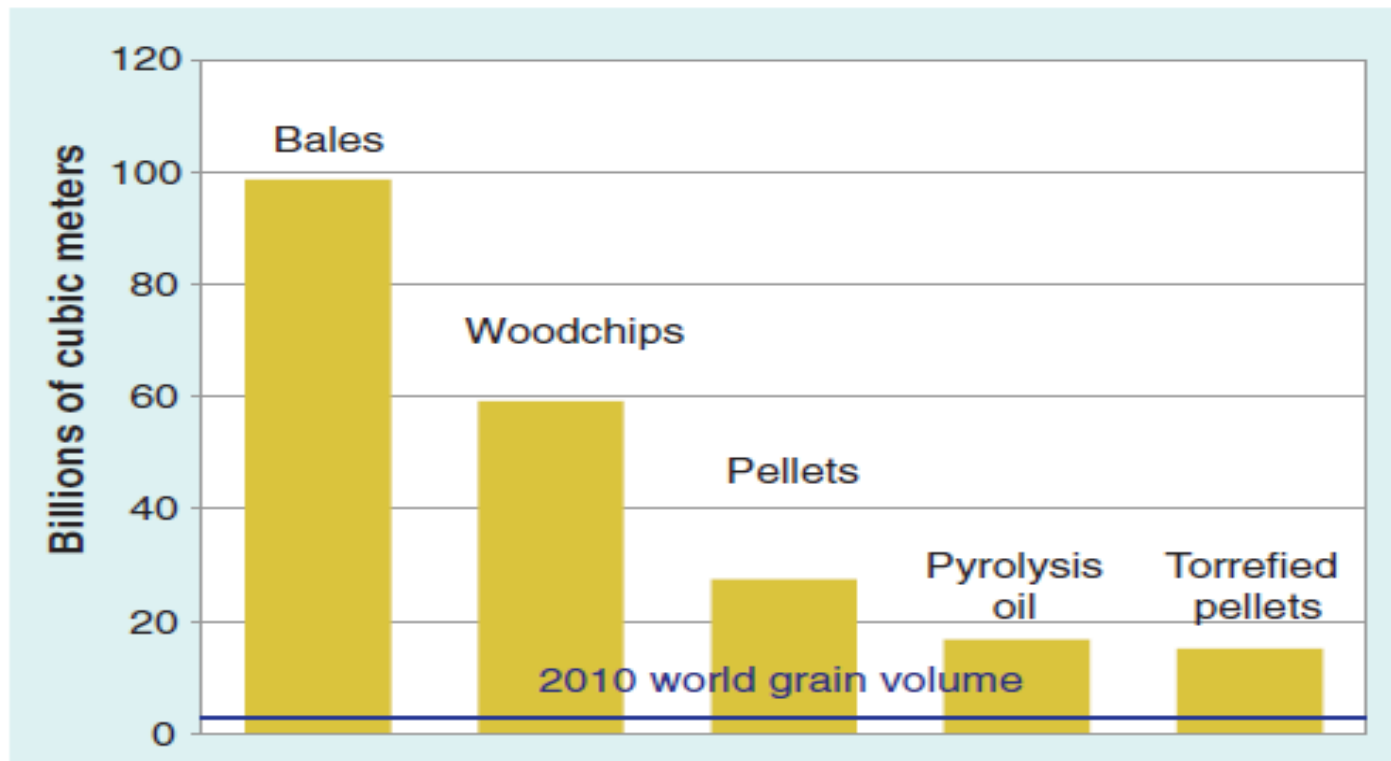


Fig. 1. Global biomass volumes required to achieve a 50% reduction in greenhouse gas emissions by 2050. A wide range of densification options are possible, but even the most effective will still require several times the biomass-handling capacity that the commodity grain system uses today.

Challenges in Scaling Up Biofuels Infrastructure

Tom L. Richard, *et al.*
Science **329**, 793 (2010);
 DOI: 10.1126/science.1189139

AFEX™ Pellets: A Versatile Biomass Commodity

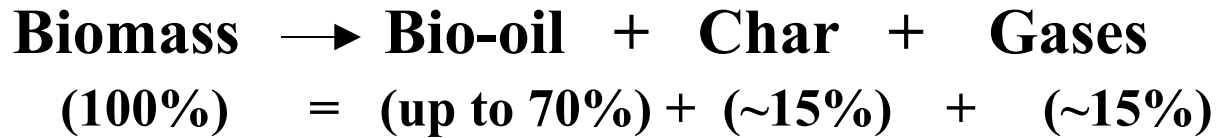


- Biorefinery sugar feedstock
- Releases 75+% of sugars for fuels and chemicals



- Ruminant animal feed for beef and dairy cattle
- Potential to displace corn grain

Saffron: Fast Pyrolysis for Biomass Liquefaction



- **Pyrolysis is thermal decomposition without oxygen**
 - **Modest energy costs:** Pyrolysis reaction temps. of ca. 500 °C
 - **Rapid throughput:** Short vapor residence time in the reactor (<1s)
 - **Densification:** Bio-oil has a higher bulk density than biomass
 - **General, carbon-retentive:** Retains most fixed carbon in liquid
- **Bio-oil unwanted properties (stabilization):**
 - Reactive and unstable: aldehydes, ketones, phenols
 - Corrosive: carboxylic acids, phenols
 - Low specific energy

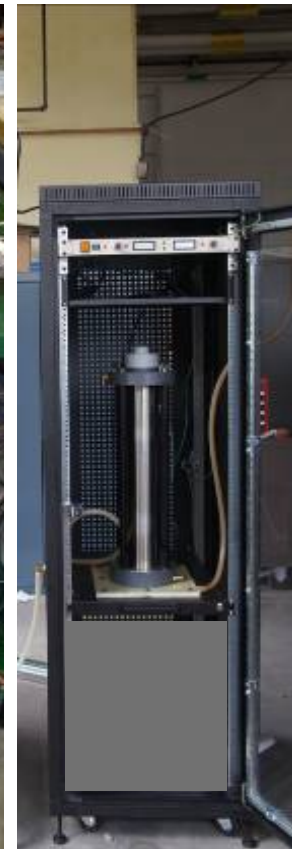
Pyrolysis Reactor



**Biomass feeder
and reactor**



**Condenser and
collection vessels**



**Electrostatic
precipitator**



**Gas flame
calorimeter**

Pyrolysis reactor/reaction products

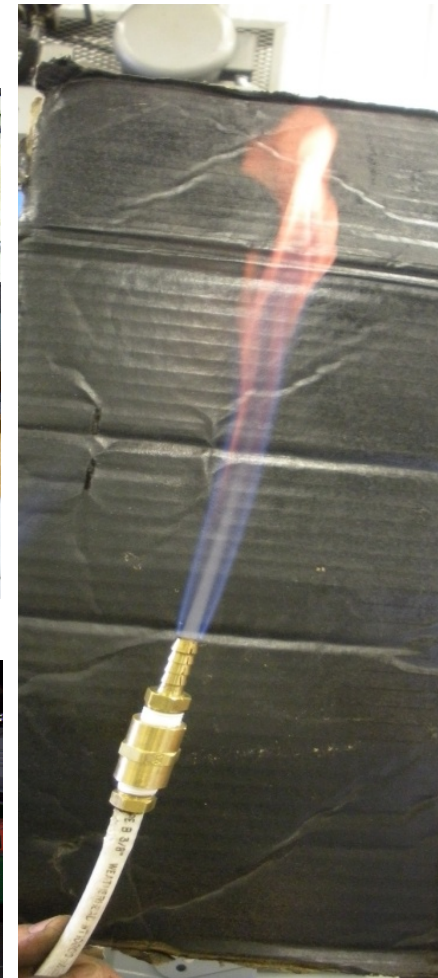


Condenser and collection vessels

Char trap

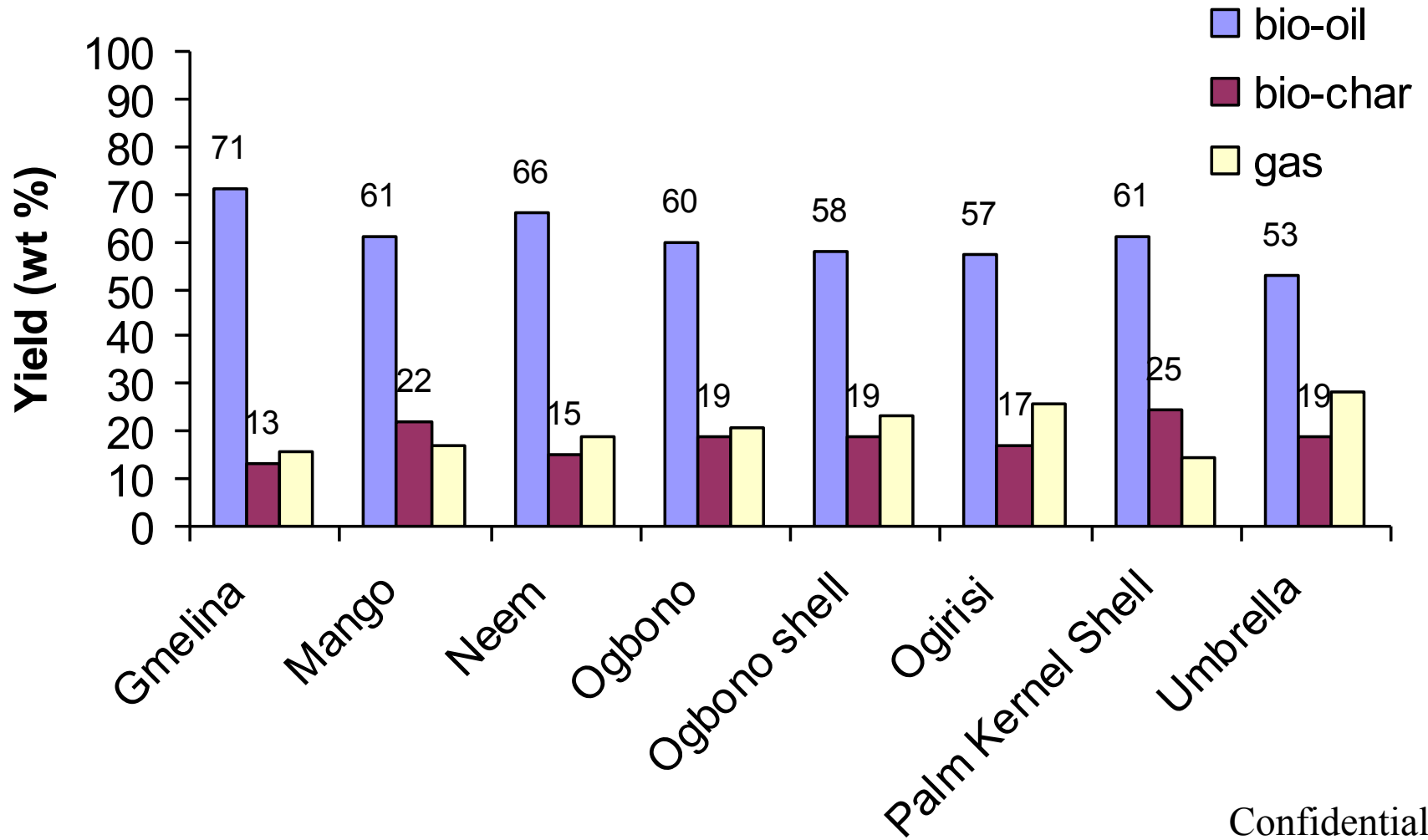


Bio-oil in traps



Non-condensed gas

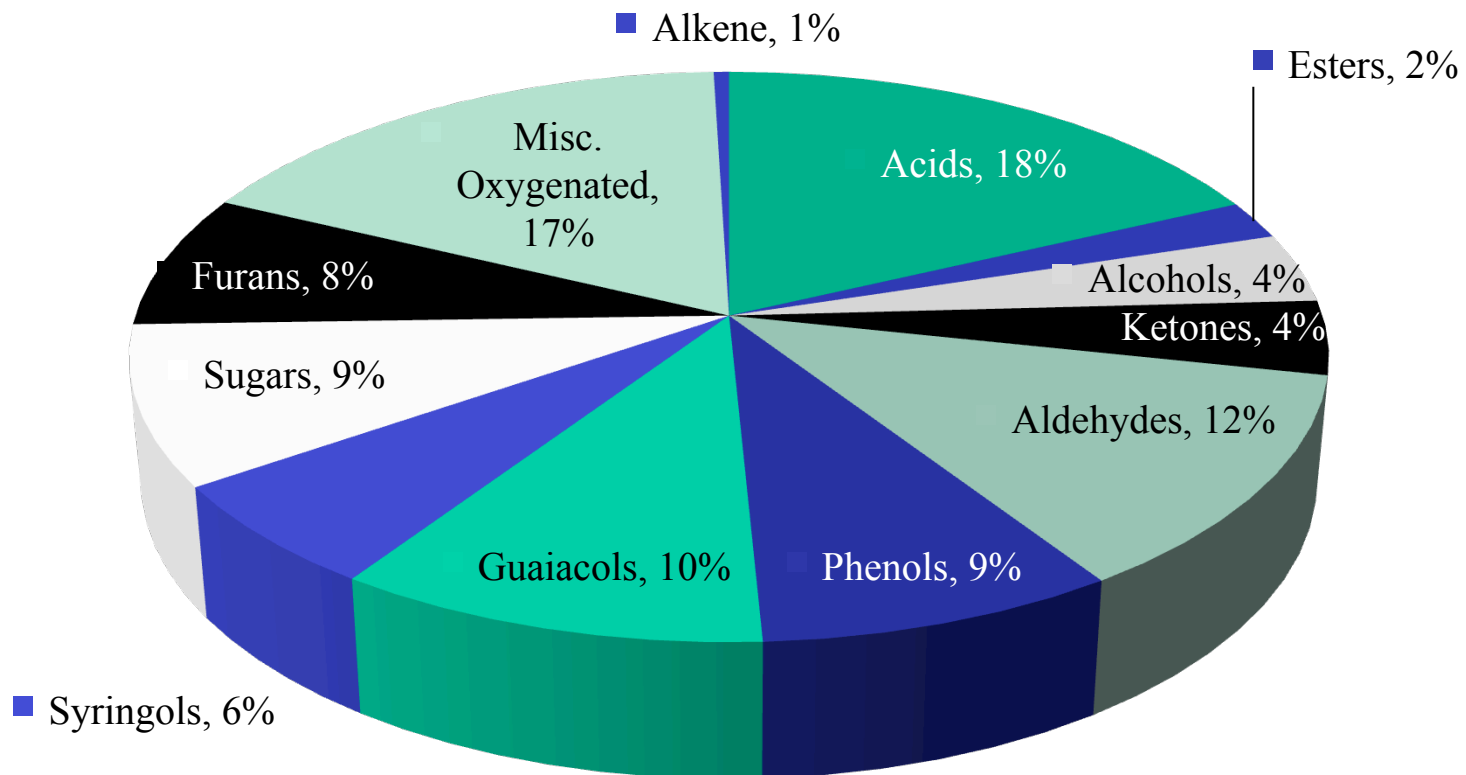
Tropical Plant Pyrolysis Yields



Confidential

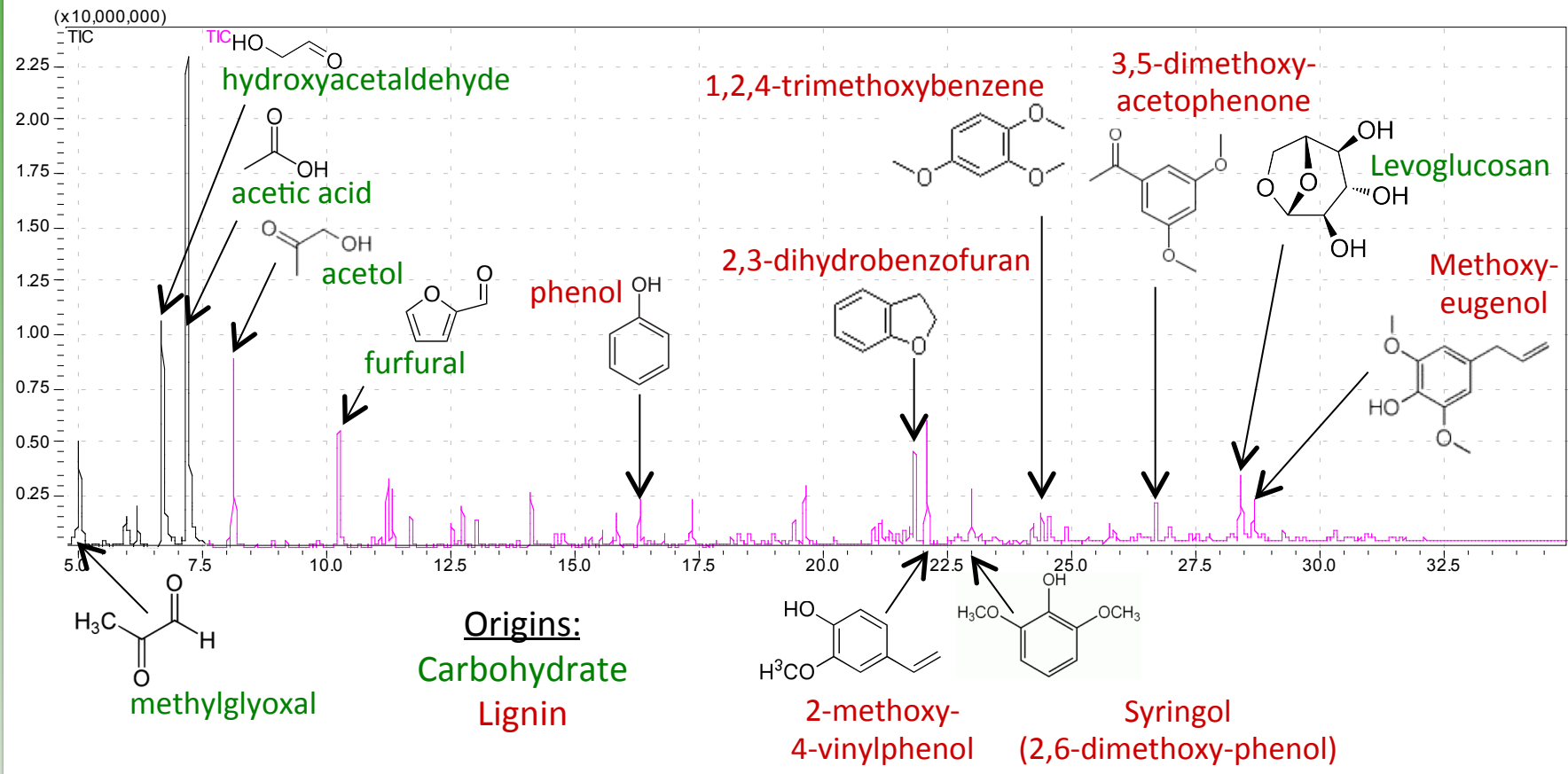
Bio-Oil Composition

General Distribution of Organic Compounds in Bio-oil

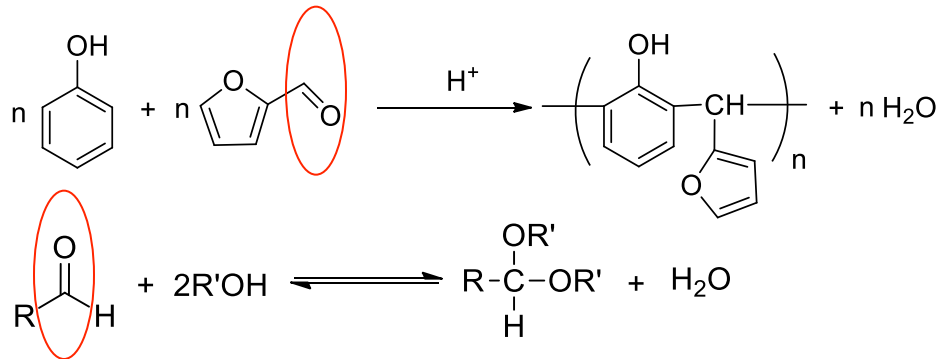
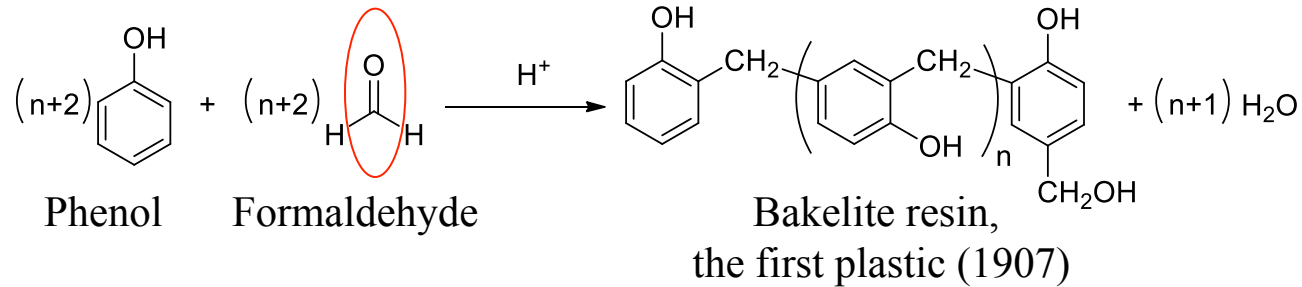


Source: Fast Pyrolysis of Biomass: A Handbook Vol. 2
A. V. Bridgewater, Ed.; CPL Press 2002

Pyrolysis of Switchgrass (500 °C) GC-MS trace



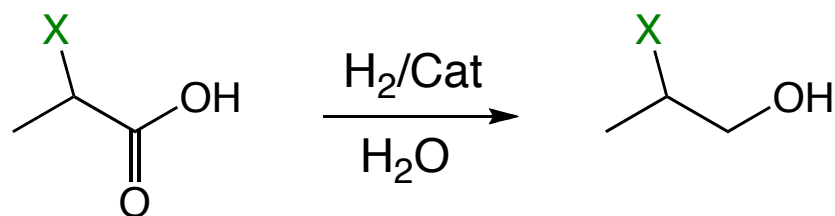
Bio-oil Storage and Transport Challenge: Reactivity and Instability



Stabilization requires reduction of carbonyl groups and of acidity

Team background: bio-based building blocks at MSU

A 20+ year collaboration of Jackson & Miller groups,
Catalytic Hydrogenation of fermentation-based cpds in H₂O



X = OH: Lactic Acid
(from starch fermentation) Propylene Glycol
(>10⁹ kg/yr commodity)

X = H: Propanoic Acid 1-Propanol + CH₄ etc.

X = NH₃⁺: Amino Acid
(from protein hydrolysis) Amino Alcohol (high-value
chiral building block)

***Pressures that are frightening to organic chemists**



1500 psi*, 150 °C
but clean, selective

Slow, unselective

1000 psi*, 120 °C,
clean, selective but
requires acid (H₃PO₄)

Lactic and Propanoic Acid:

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

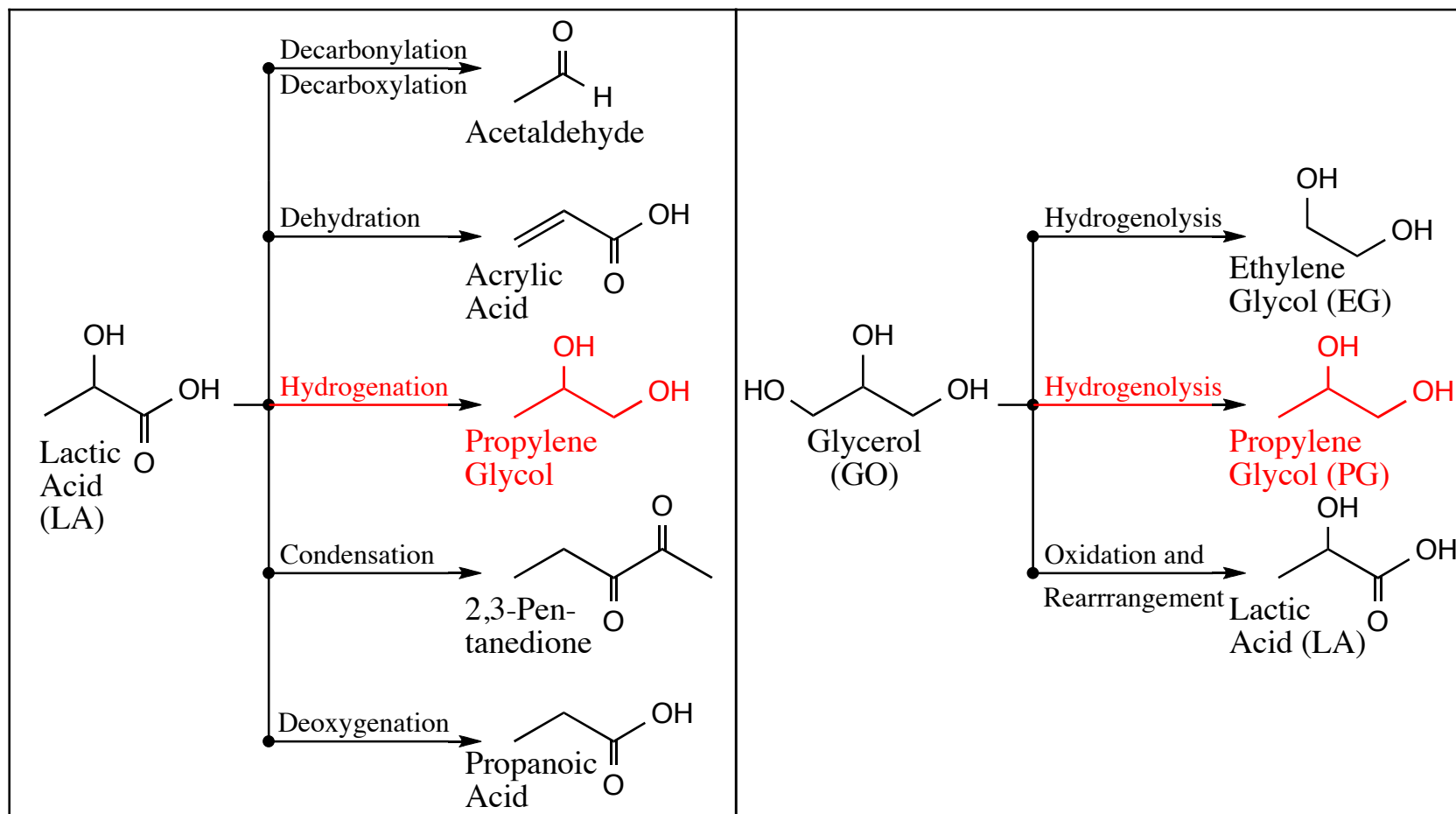
with Y. Xi, D. J. Miller, *Ind. Eng. Chem. Res.* **2011**, 50, 5440-5447.

Inhibition: with Z. Zhang, D. J. Miller, *Biores. Tech.* **2008**, 99, 5873-5880.

Alanine and other Amino Acids:

Kinetics: with K. Pimparkar, D. J. Miller *Ind. Eng. Chem. Res.* **2008**, 47, 7648-7653.

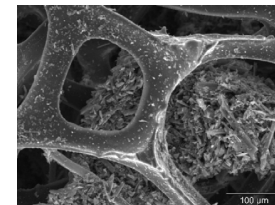
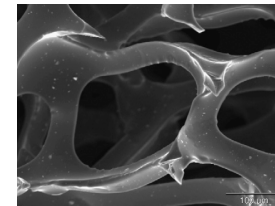
Biorenewable Platforms: Lactic Acid and Glycerol



High pressure, high temperature, stainless steel batch reactors

Electrocatalytic Hydrogenation (ECH): Electricity as a Chemical Reagent

- Overcomes low H_2 solubility in H_2O by forming H_2 on catalytic metal
- Enables hydrogenation of hard substrates at **room P** & (surprise!) **modest T**.
- Electric power sources:
 - Traditional sources: **Non-liquid** (coal, NG) fossil fuels, Hydro, Nuclear
 - Fast-growing C-neutral sources: **Solar, Wind, Tidal hydro**
- With research galloping toward higher efficiency, lower cost PV and wind technologies, electricity is evolving into a primary energy form, but...
- Capture, storage, distribution remain inefficient
- Conversion of **locally captured** electric E into fuels addresses two needs:
Fuel synthesis and energy storage
- Splitting H_2O , so anode chemistry critical; use Nocera's $CoPO_4$



MSU research reactor

Targeting Liquid Hydrocarbons: A closer look

Boundary conditions due to scale of human fuel use:

- **Liquid hydrocarbons** are the fuel of the past ... and the future
 - Unbeatable Energy vs. weight ratio
 - “Nature’s choice” across the tree of (mobile) life
- **Oil:** EIA says 1×10^9 tonnes/year of oil used in US; this is ca. 1/5 world usage
 - C content in “CH₂” is 12/14 or 86%, so 860×10^6 tonnes C/year
 - E content: Alkanes @ 45 MJ/kg --> 45×10^{18} J/year
- **Biomass:** USDA says 1.5×10^9 tons/year of non-food biomass could be gathered (crop residues, forest wastes, and energy crops)
 - C content in “CHOH” is 12/30, or 40%, so 600×10^6 tons/year
 - E content: Biomass @ 15 MJ/kg --> 23×10^{18} J/year (assuming perfect conversions)
- **Today’s biofuels:** Consider ethanol production:
 - $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH$ (MW = 46) + $2CO_2$ (MW = 44)
 - Concentrates plant-captured E into half the mass, but throws away 1/3 of the C
 - E content: Ethanol doesn’t come close to a 1:1 gasoline or diesel replacement
- Plants are poor (~1%) at capturing solar E; Human tools are $\geq 10x$ better but...
 - They all make electricity ==> **Electrocatalytic hydrogenation is our destiny!**

The Energy and Carbon Problems

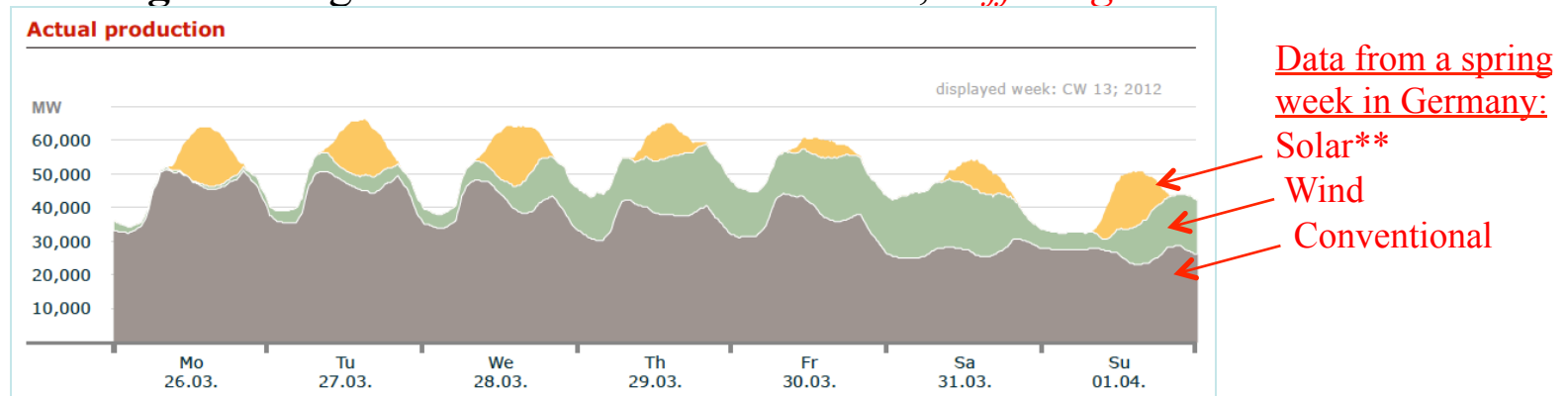
- At base, biomass-to-energy strategies are **solar energy capture schemes**
- Making practical liquid fuels (i.e. hydrocarbons) renewably also requires a scheme for **carbon capture and retention**
- Compare plant and human technologies:
 - **Energy: Plants** are poor (ca. **1% efficient**) at capturing 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 is, all these technologies produce their energy as **electrical power**.
 - **Carbon:** Plants are undisputed champions at capturing the very dilute CO₂ from the atmosphere. No serious human technology even tries.
- *Let plants do what they do best--capture C from a very dilute supply*
- *Let humans do what we do better--capture E from plentiful sunlight*
- *Then energy upgrade all biomass carbon rather than wasting it*
- *Simple, general strategies that minimize unnecessary chemical restructuring and processing steps will be essential*

Some questions:

- Why focus on liquid hydrocarbons? Isn't this just an overall energy problem?
 - $F = ma$; High energy/mass ratio is critical for transportation fuels, as evolution illustrates. Weight is wasteful.
- Why pyrolysis (not e.g. hydrolysis/fermentation, gasification/F-T synthesis, etc.)?
 - Need midsize fragments, at low Energy/H₂O cost, for fuels.
 - Low E, C content in biomass requires E upgrading to maximize yield.
- Why upgrade locally vs. sending directly to refineries?
 - Transportation costs of hauling dilute fuels are high.
 - Refineries don't handle feedstocks with high oxygen contents well.
- Why make fuels by electrolytic processing?
Today we *burn* fuels to make electricity!
 - Liquid hydrocarbons are extra valuable as both fuels & feedstocks.
 - Carbon-free sources make electricity, but out of sync with demand.
 - Future refining will need these tools to link energy technologies.

Facts and Figures, Summer 2012: Solar and Wind Power

- **Timing:** Power generation not matched to load; *buffering is needed*

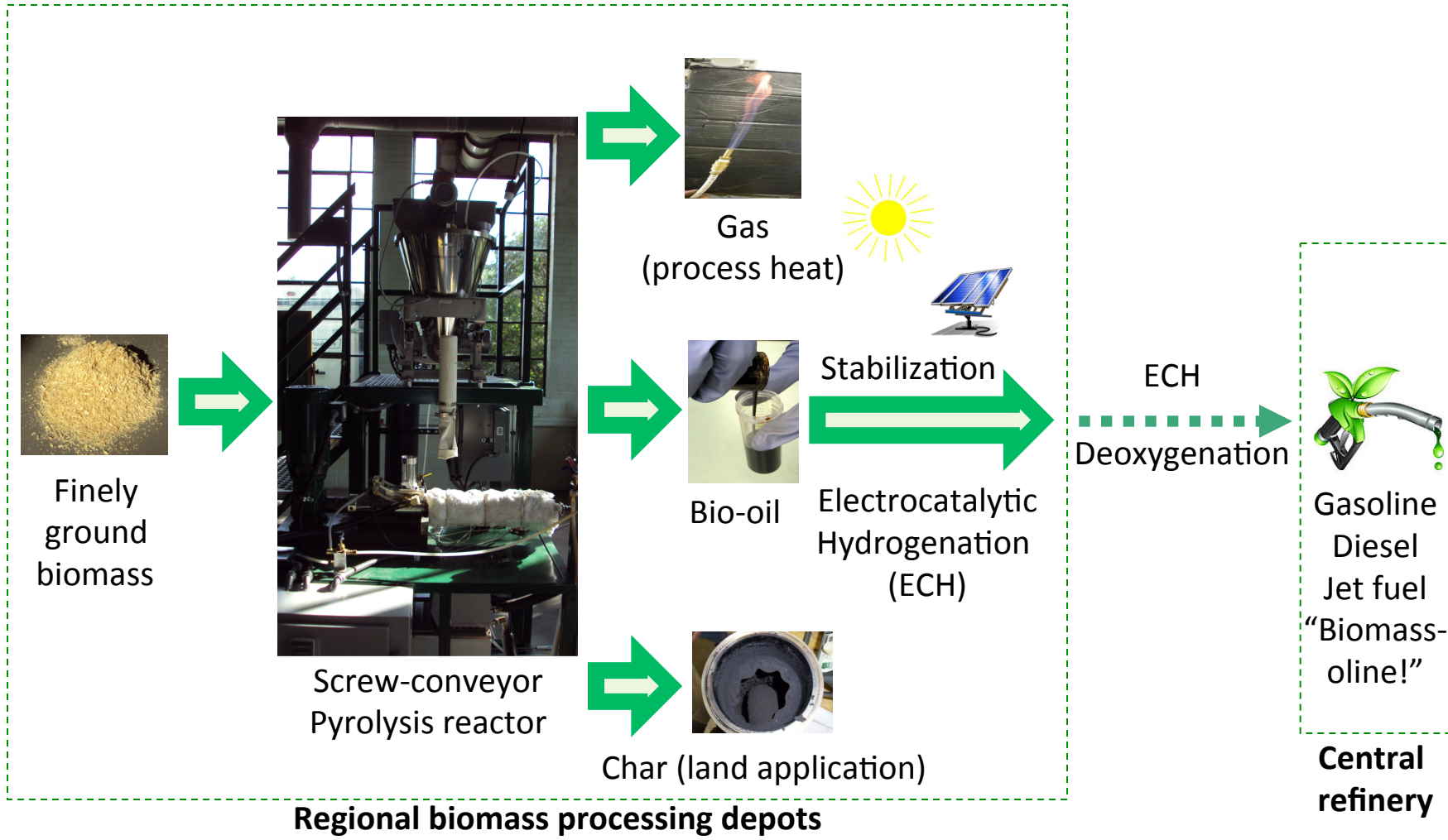


- **Costs:** Comparisons sensitive to capital (amortization) vs. operating calcs
- **Land use:** Typical PV efficiencies ca. 15%, *much* higher than the best biomass
- **Implementation:** PV: US: < 0.5%; DE: ca. 5%; Wind: US: 3%; DE: 10%
- **Growth:** Double digit annual growth in both PV and wind power installations

*U.S. EIA and IEA data

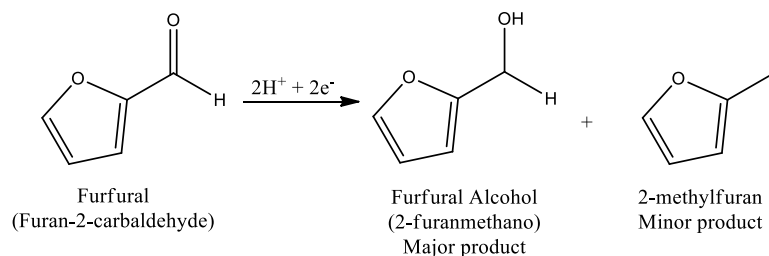
**Graphic from July 23, 2012 presentation by Burger, Bruno; Fraunhofer Inst. for Solar Energy Systems, www.ise.fraunhofer.de, accessed 29 July 2012

Grand Scheme: Fast Pyrolysis and Electrocatalytic Upgrading

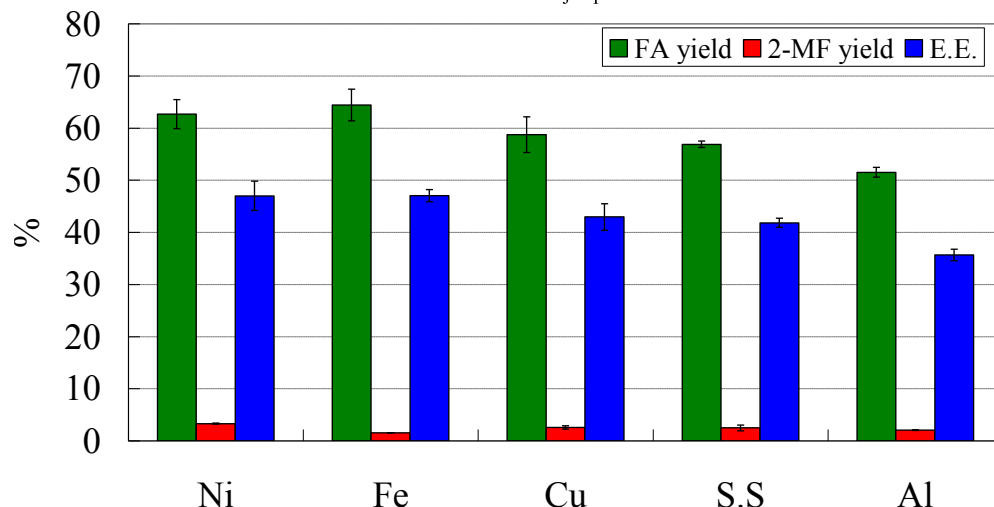


Furfural reduction:

Explore yield and current efficiency vs. cathode metals, pH, [substrate], cell configuration & current density

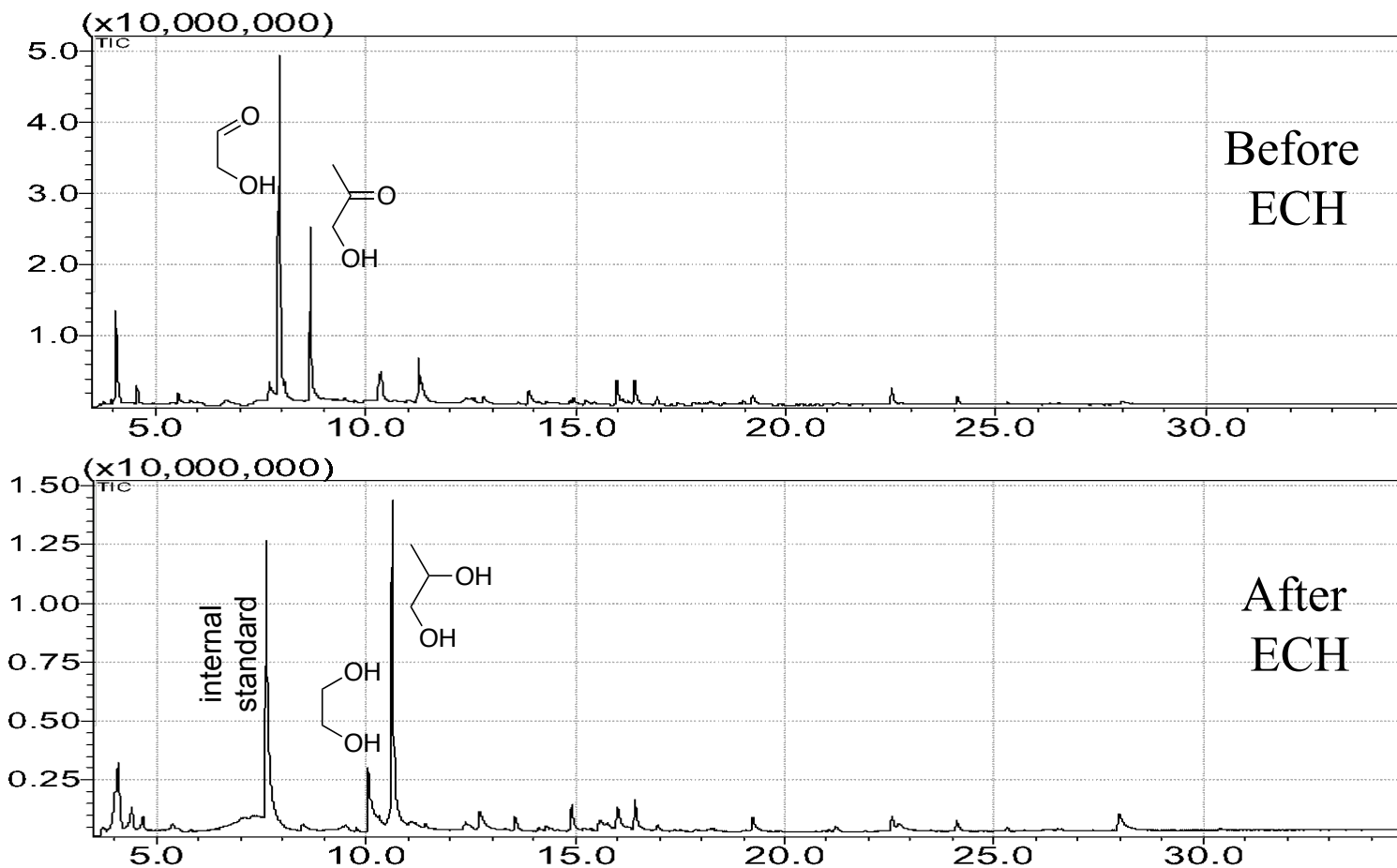


Low pH favors 2-MF, but only up to ca. 8%.

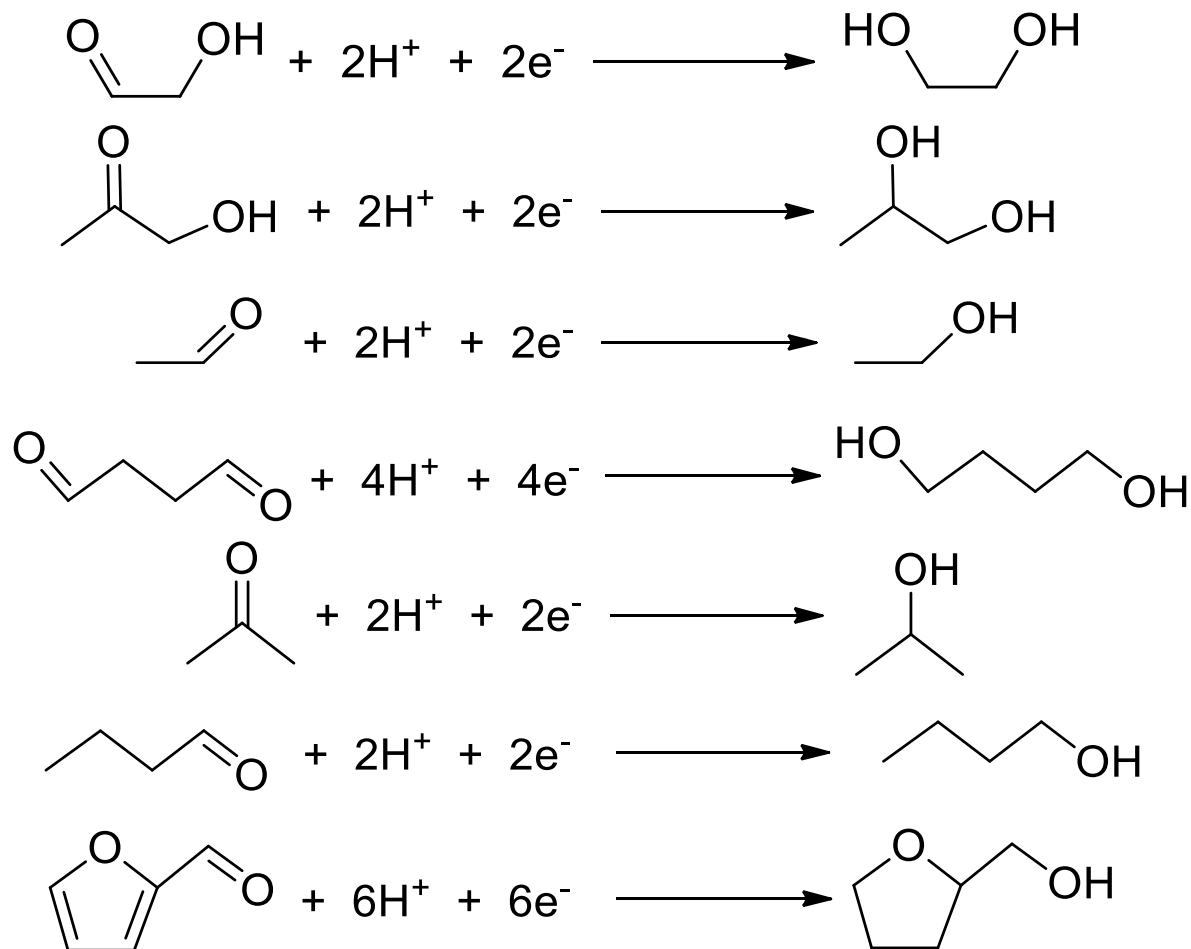


...with Zhenglong Li, Shantanu Kelkar, Chun Ho Lam, Kathryn Luczek
Electrochimica Acta **2012**, 64, 87– 93.

ECH to stabilize water-soluble bio-oil

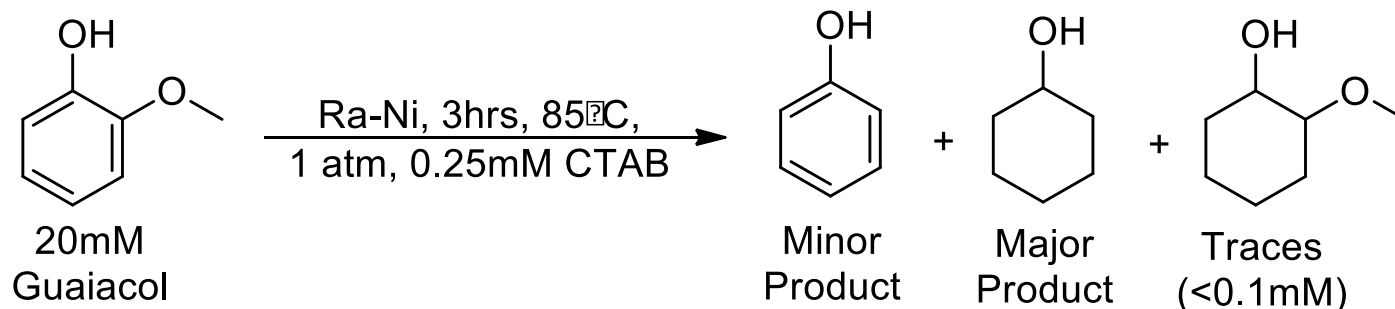


ECH of Water-soluble Bio-oil: Carbonyl reductions



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

Lignin reactions: Raney Ni favors demethoxylation first!

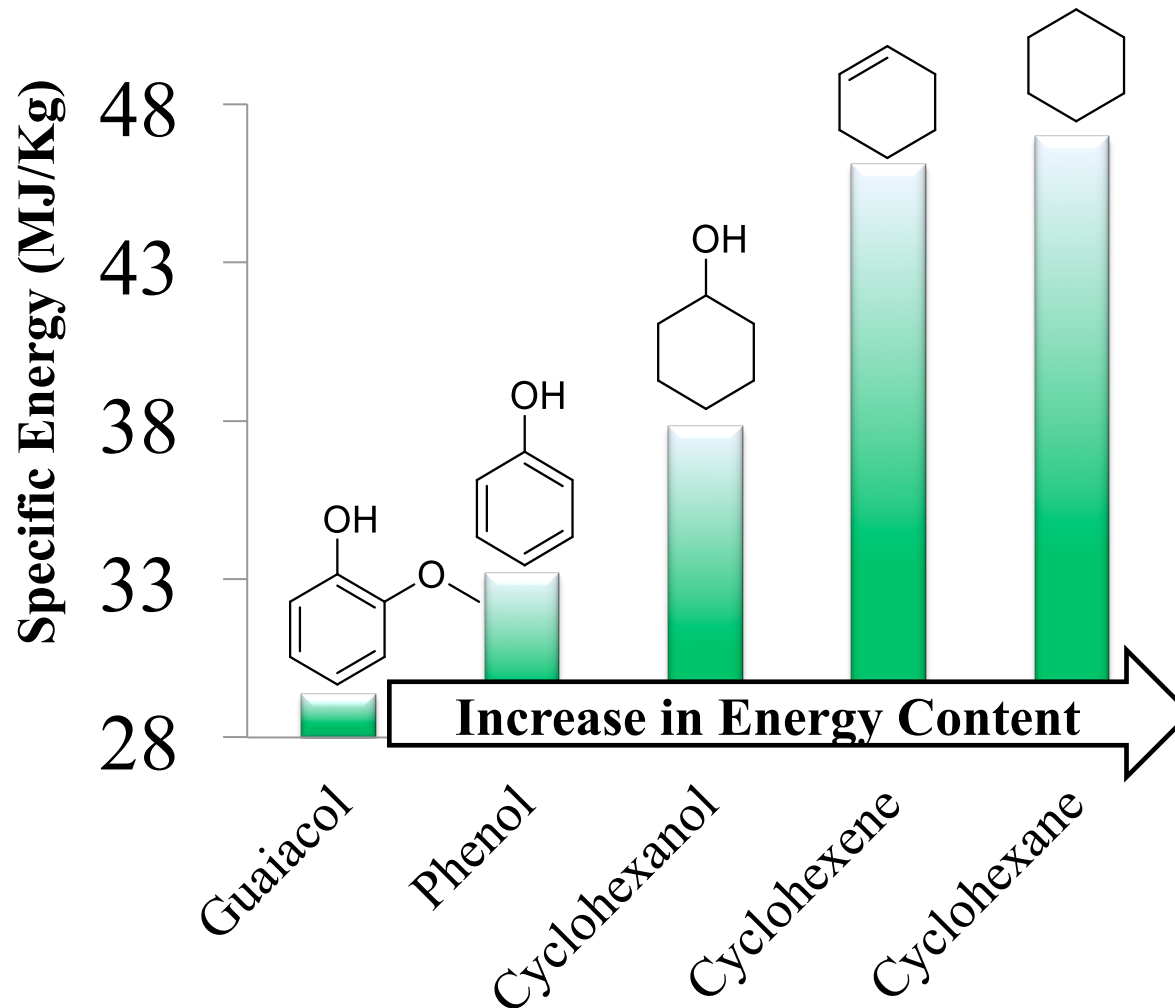


Electrolyte Buffer	Unreacted Guaiacol (%)	Phenol (%)	Cyclohexanol (%)	Material Balance (%)	C.E. (%)
pH 2.0, 1.0 M HCl/KCl	10.9	12.7	34.3	57.9	31.6
pH 2.0, 0.2 M HCl/KCl	43.0	17.4	24.3	84.8	28.6
pH 4.0, NaOAc	32.7	13.9	17.0	63.5	14.7
pH 8.0, NH ₄ OAc	62.0	9.0	0.6	71.5	2.4
pH 8.0, K Borate	0.63	3.20	19.2	81.0	23.3

...with Zhenglong Li, Mahlet Garedew, Chun Ho Lam
Green Chem. **2012**, *14*, in press, DOI: 10.1039/c2gc35552c

Ketones and aldehydes are easy; target lignins:

Energy content vs. extent of hydrogenation



Importance of Low-cost Catalysts:

Cathode side: ECH with Raney Nickel

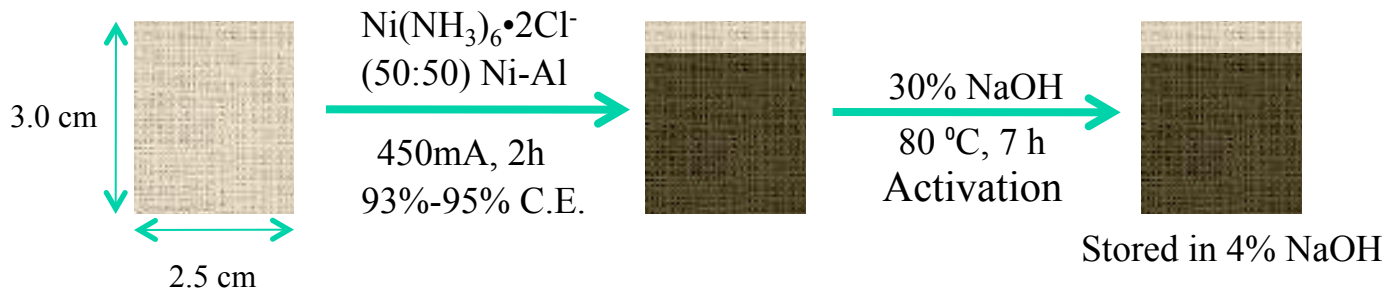
Anode side: Water splitting with Nocera CoPO_4 catalyst

- Raney Ni cathode:
 - Advantages:
 - Nickel ~\$20/kg vs. Ruthenium ~\$3,200/kg
 - Nickel is easy to reduce/ Simple Preparation
 - Challenges:
 - Nickel is less active towards aromatics than Ruthenium
 - Surfactants, organic co-solvent may be required to aid reaction
 - Nickel has a low Hydrogen Evolution Potential → Makes H_2 easily.

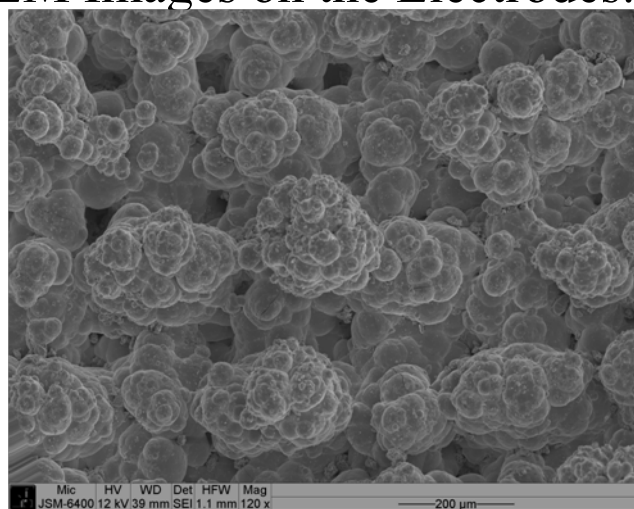
- CoPO_4 anode:
 - Advantages:
 - Cobalt ~\$50/kg vs. Platinum ~\$45,000/kg
 - Self assembles from salts in solution
 - Challenges:
 - Oxidizes phenolic compounds to make a passivated coating
 - Cobalt cations may cross membrane

Preparation of Raney-Nickel Cathode

Raney-Nickel on Stainless Steel:

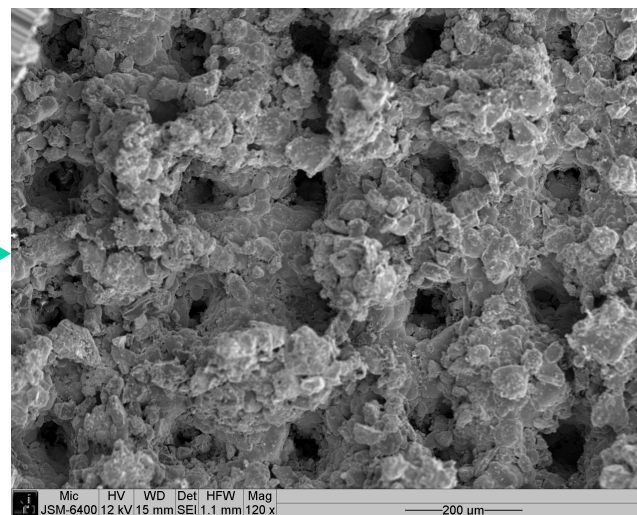


SEM Images on the Electrodes:



Before Activation

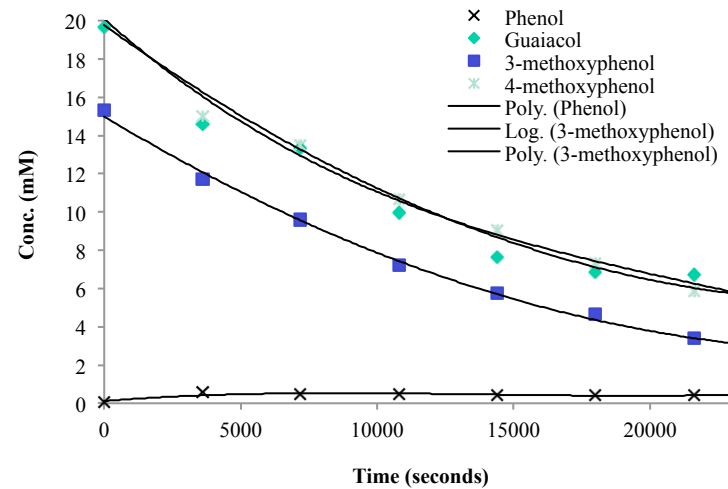
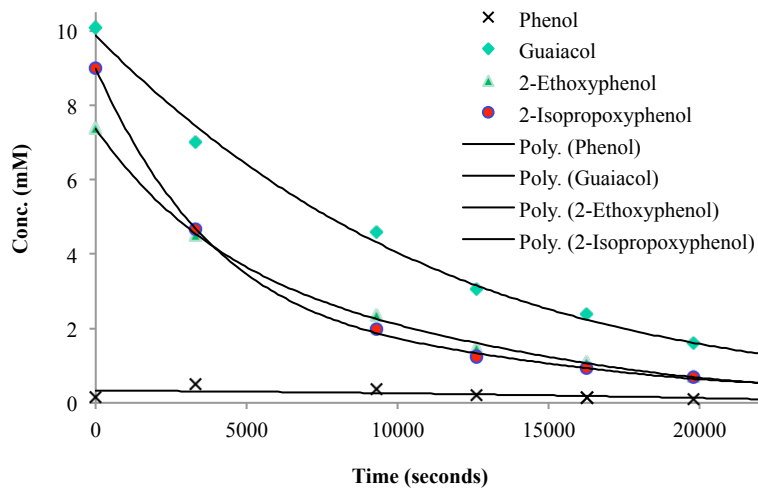
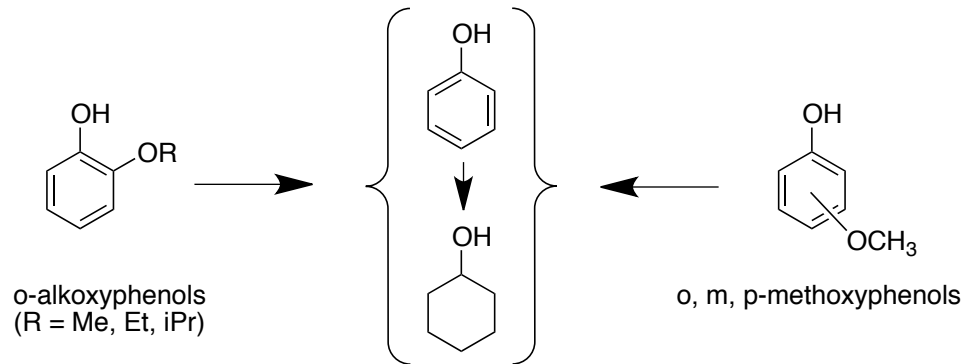
30% NaOH
80 °C, 7 h



After Activation

H. Ilikti.; N. Rekik.; M.J. Thomalla, *J. Appl. Electrochem.* **2002**,32, 603-609.

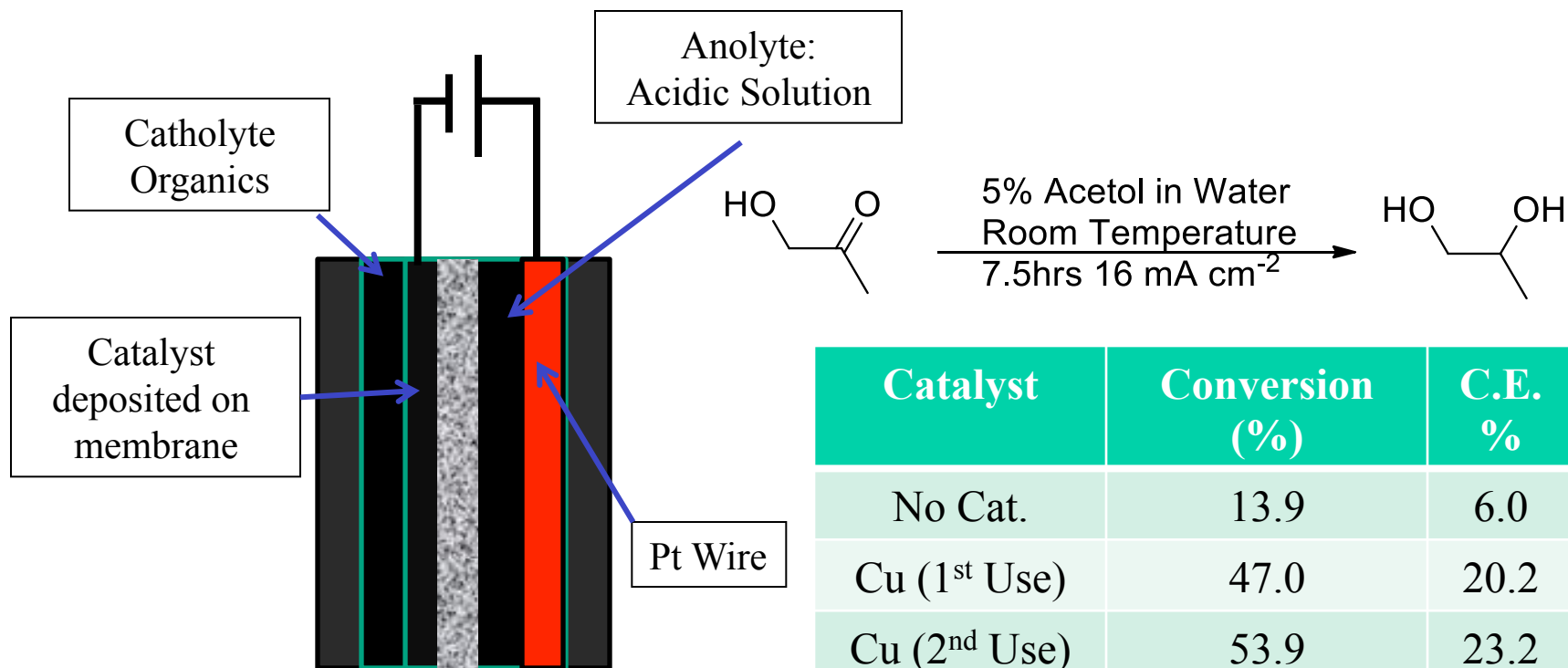
Generalizing the Raney Ni ether cleavage:



Jason Lam

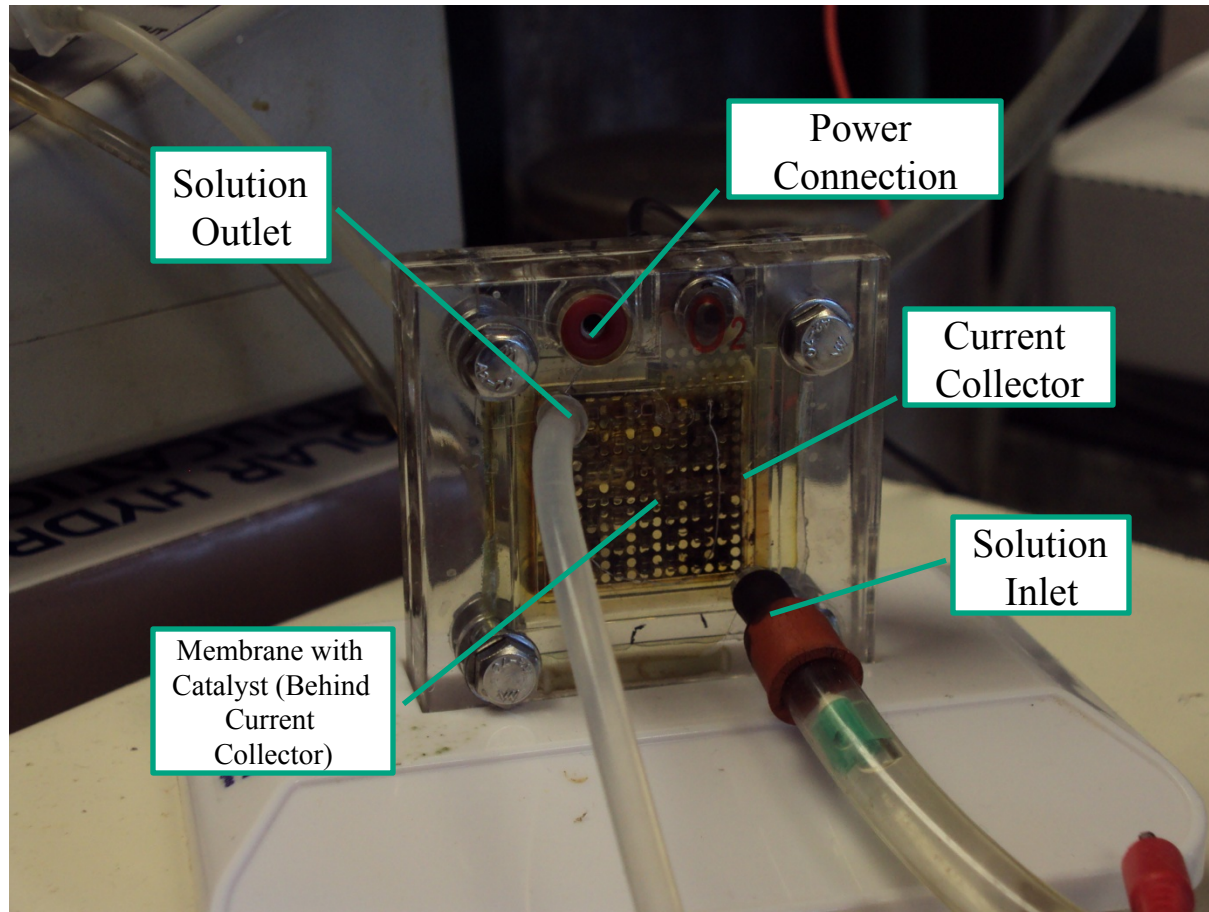
Solid Polymer Electrode

Applications in Organic Reductions



Catalyst	Conversion (%)	C.E. %
No Cat.	13.9	6.0
Cu (1 st Use)	47.0	20.2
Cu (2 nd Use)	53.9	23.2
Cu (3 rd Use)	13.0	5.6
Pt	51.2	22.0
Ru	48.49	28.6

Next generation reduction cell setup: “inverse fuel cell”



Biomass Deconstruction, Conversion, and Upgrading to Fuels

Biomass



Pretreatments

AHP/enzyme
AFEX
E-AFEX

Chemical conversion



Chemically Tractable Biomass carbon
(polyols, aromatics)

Liquefaction
Pyrolysis

Energy Upgrading
ECH, hydrotreating

**Liquid Fuels
Chemicals**

