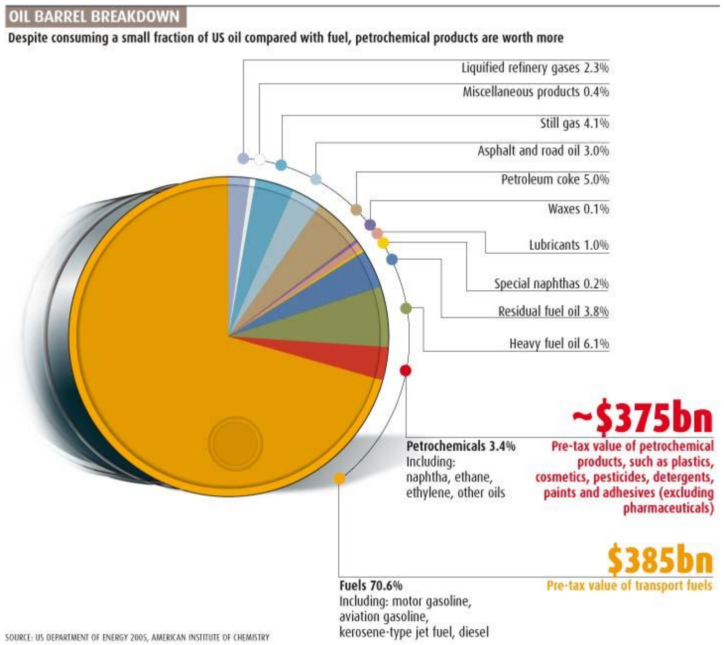

# Engineering Research Center

# Biorenewable Chemicals

**Peter L Keeling**

# Petro-based

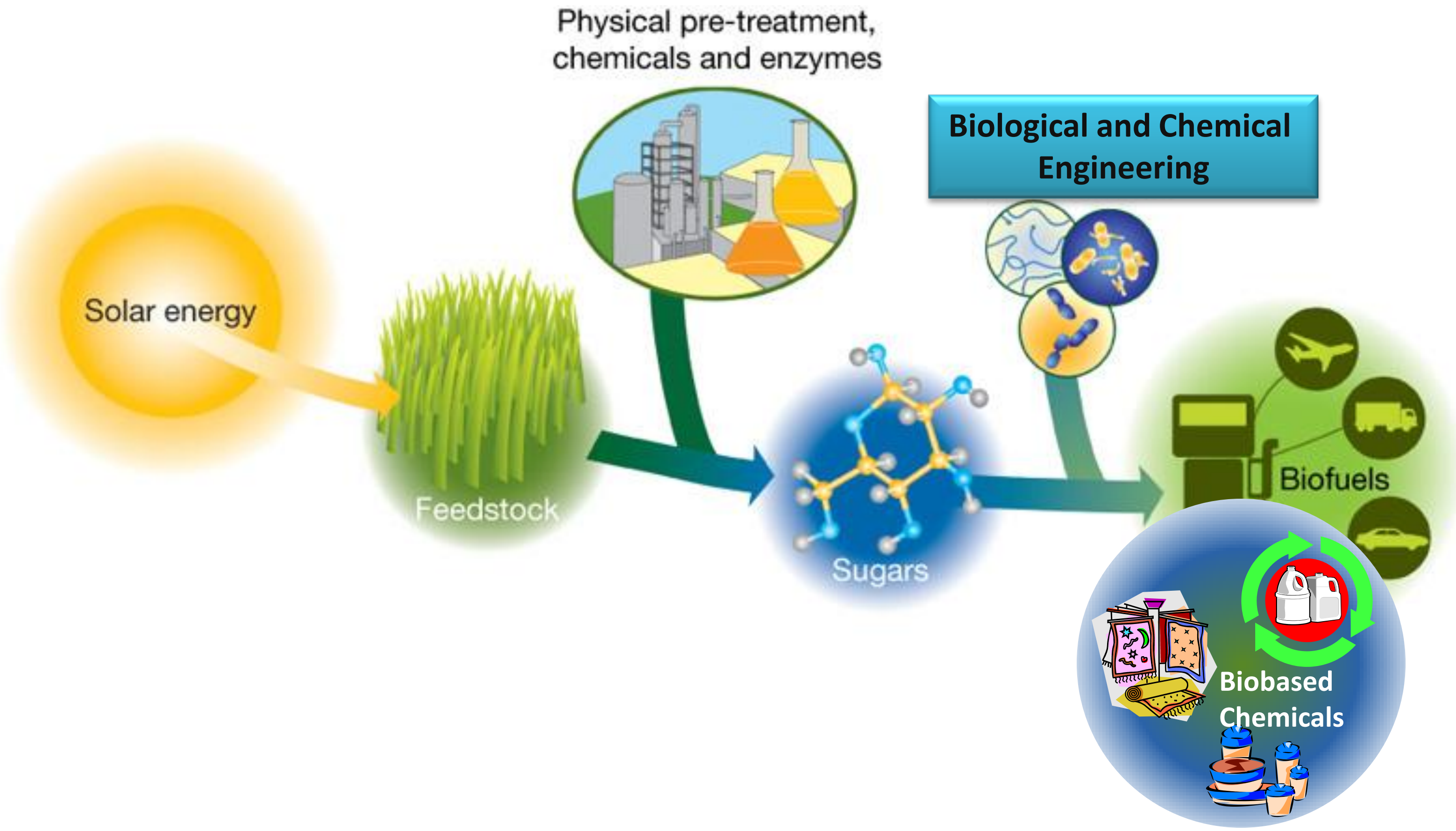




**An array of bio-based opportunities:**

- **Polymers, Paints, Coatings, Resins, Industrial Chemicals**
- **Packaging, Bottles, Containers, Inks, Dyes**
- **Adhesives, Sealants, Construction Chemicals**
- **Surfactants, Cleaning Agents, Specialty Chemicals**
- **Food additives, Flavorings, Fragrances, Cosmetics**

# Bio-based

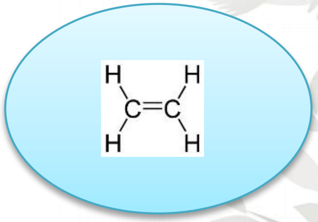




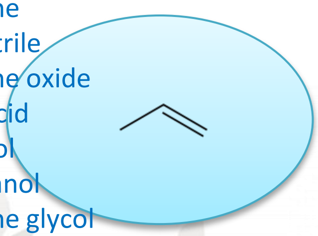
Adapted from: http://climate-connections.org

# Challenge

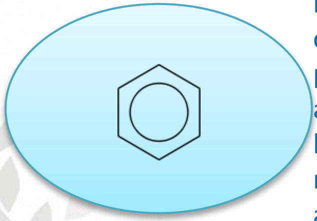
**ETHYLENE**
maleic anhydride
ethanol
ethylene
ethylene dichloride
vinyl chloride
ethylene oxide
ethylene glycol
a-olefins
vinyl acetate
ethanolamines
diethylene glycol
butene-1
1,4-butanediol

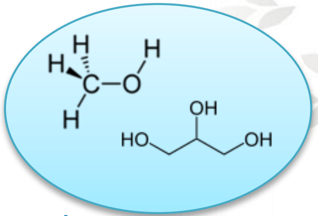



**PROPYLENE**
propylene
acrylonitrile
propylene oxide
acrylic acid
n-butanol
isopropanol
propylene glycol
2-ethylhexanol
methyl ethyl ketone

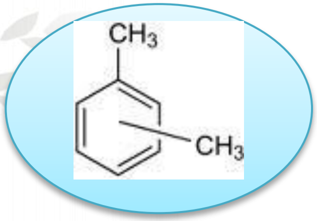


**BENZENE**
benzene
nitrobenzene
cyclohexane
adipic acid
caprolactam
linear alkylbenzene
cumene
phenol
acetone
bisphenol-A
methyl diphenyl diisocyanate
aniline
ethylbenzene
styrene






**METHANOL/GLYCEROL**
glycerol
methanol
methyl tert-butyl ether
formaldehyde
acetic acid
methyl chloride
Chloroform
methyl methacrylate



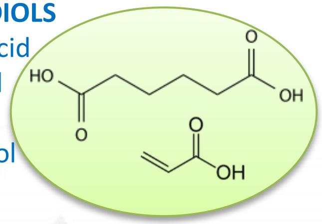

**XYLENE**
toluene diisocyanate
phthalic anhydride
o-xylene
terephthalic acid
p-xylene
butadiene

**Alkanes/Cycloalkanes/Aromatics**

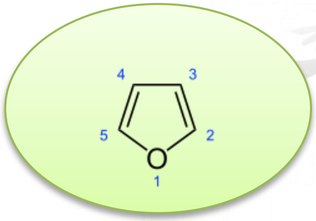
# Opportunity



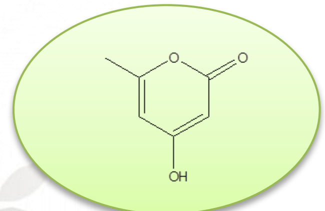
**DIACIDS/DIOLS**
Succinic Acid
Adipic Acid
Butanediol
Propanediol




Diacids/Diols

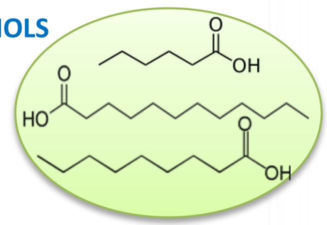



Furan Rings

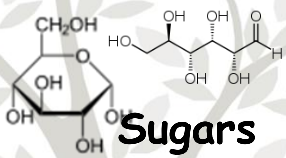



Pyrone Rings

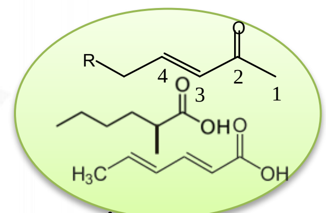
**ACIDS/ALCOHOLS**
Lactic Acid
Acrylic Acid



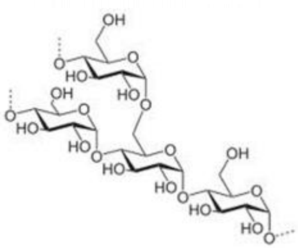

Acids/Alcohols



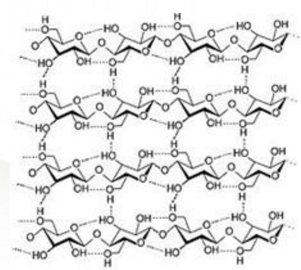

Sugars



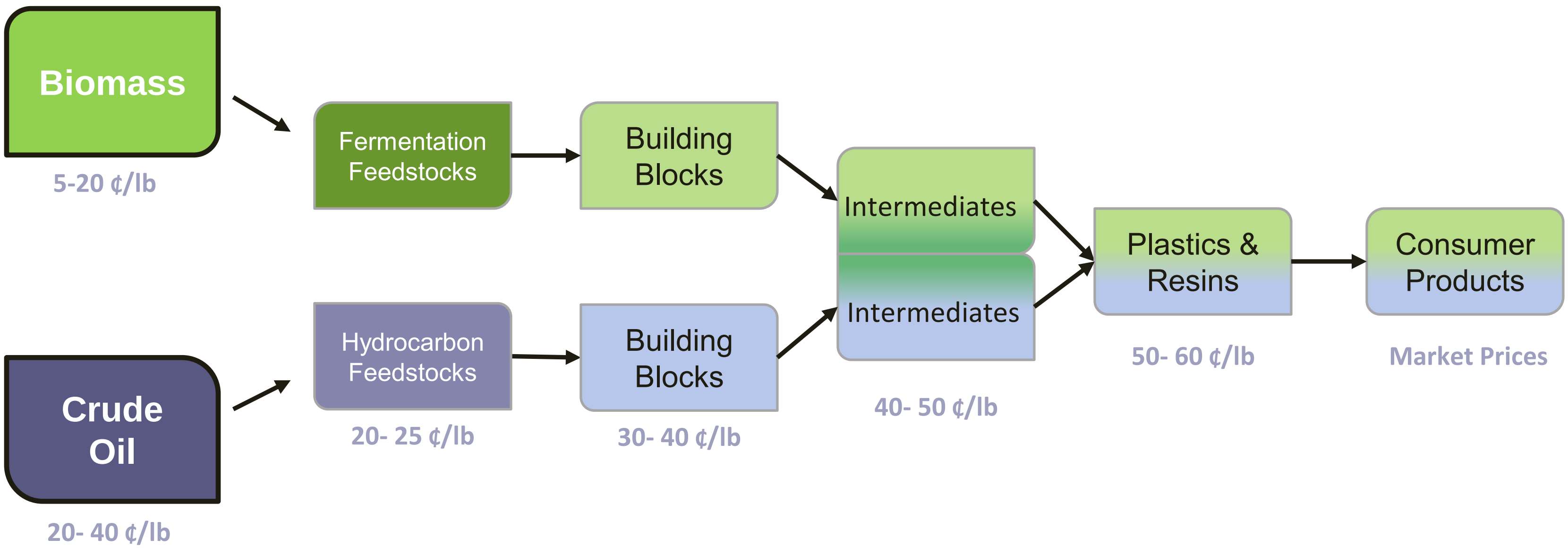

Multifunctionals



Starch / Cellulose



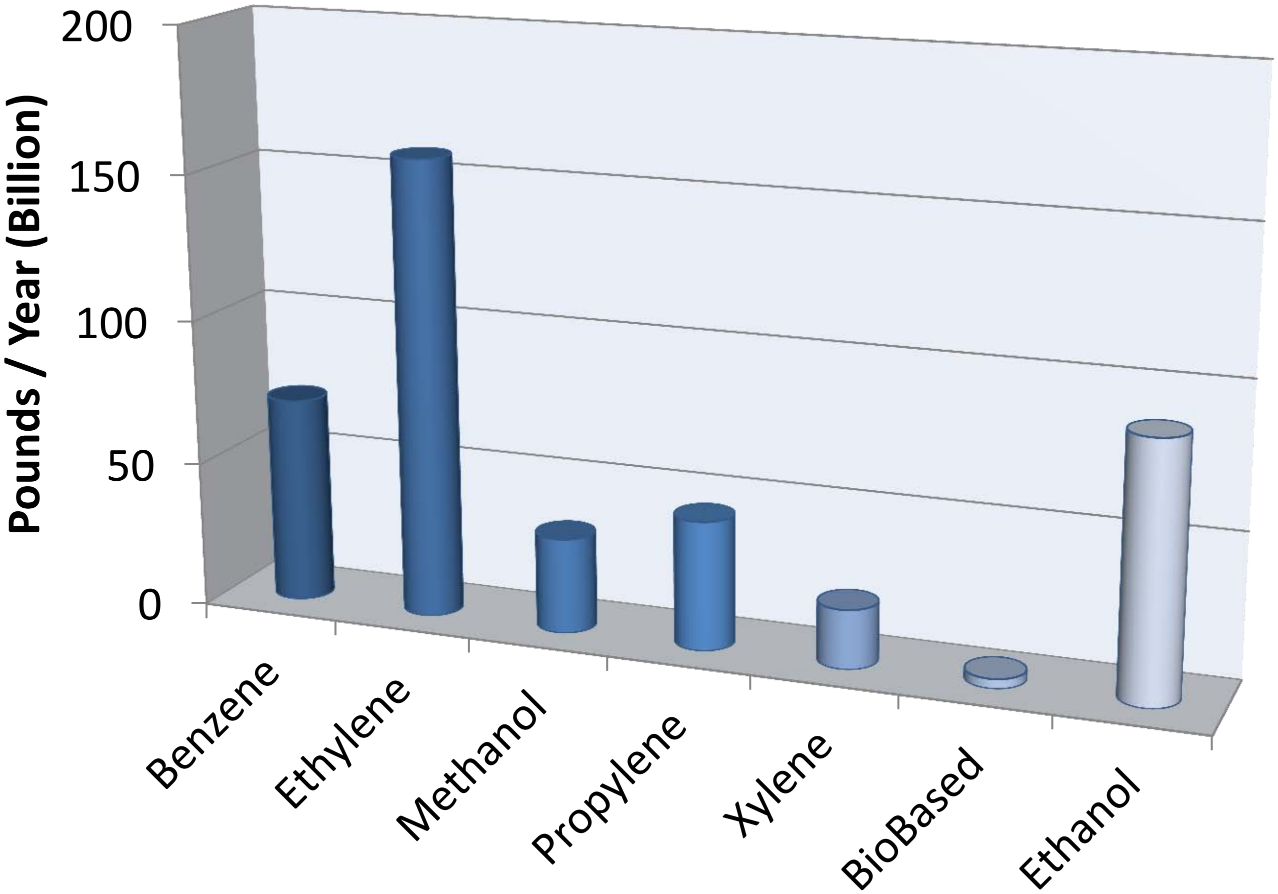
# Risk




IHS 2012:
Light Naphtha – 47 c/lb
Naphtha Ethylene – 69 c/lb
Shale Gas Ethylene – 18 c/lb

Adapted from: PetroleumOnline.com

# Scale


Pounds / Year (Billion)
200
150
100
50
0
Benzene
Ethylene
Methanol
Propylene
Xylene
BioBased
Ethanol

# CBiRC Partnership

CBiRC
NSF Engineering Research Center for Biorenewable Chemicals

IOWA STATE UNIVERSITY

The University of New Mexico

University of Virginia 1819

The University of Wisconsin Madison

RICE

The University of Michigan 1817

UCIrvine
University of California, Irvine

Salk Institute for Biological Studies

PennState 1855

TU/e Technische Universiteit Eindhoven University of Technology

DTU

Åbo Akademi University

Allylix

Ashland
With good chemistry great things happen.™

BASF
The Chemical Company

Chevron Phillips Chemical Company LLC

DSM
Bright Science. Brighter Living.

Danisco
First you add knowledge...

Elevance™

Endicott Biofuels, LLC
A Cleaner Alternative

Evonik Industries

Frontline Bioenergy LLC

genomatica
sustainable chemicals

Glucan Biorenewables

GlycosBio®

GPC

IFF International Flavors & Fragrances Inc.

Lesaffre Group

mbi
De-Risking and Scale-Up of Bio-Based Technologies

Michelin

NCAUR
Where the future is Created
USDA ARS United States Department of Agriculture Agricultural Research Service

NIDUS

opxbio
good chemistry.

Pine Creek Systems

POET®

solazyme®

The BioBusiness Alliance of Minnesota™

TORAY
Innovation by Chemistry



NSF

# CBiRC Faculty

### *New Biocatalysts for Pathway Engineering*

**Joe Noel *(Salk) - Lead***
Basil Nikolau *(ISU)*
Eran Pichersky *(UMich.)*
Tom Bobik *(ISU)*
Peter Reilly *(ISU)*
Eve Wurtele *(ISU)*

### *Microbial Metabolic Engineering*

**Jackie Shanks *(ISU) - Lead***
Nancy Da Silva *(UCIrv.)*
Julie Dickerson *(ISU)*
Ramon Gonzalez *(Rice)*
Laura Jarboe *(ISU)*
Costas Maranas *(PSU)*
Ka-Yiu San *(Rice)*
Suzanne Sandmeyer *(UCIrv)*
Zengyi Shao *(ISU)*

### *Chemical Catalyst Design*

**Robert Davis *(UVa) - Lead***
Brent Shanks *(ISU)*
Jim Dumesic *(UWisc)*
Abhaya Datye *(UNM)*
Matt Neurock *(UVa)*
George Kraus *(ISU)*
Klaus Schmidt-Rohr *(ISU)*
Keith Woo *(ISU)*
Jean-Philippe Tessonnier *(ISU)*

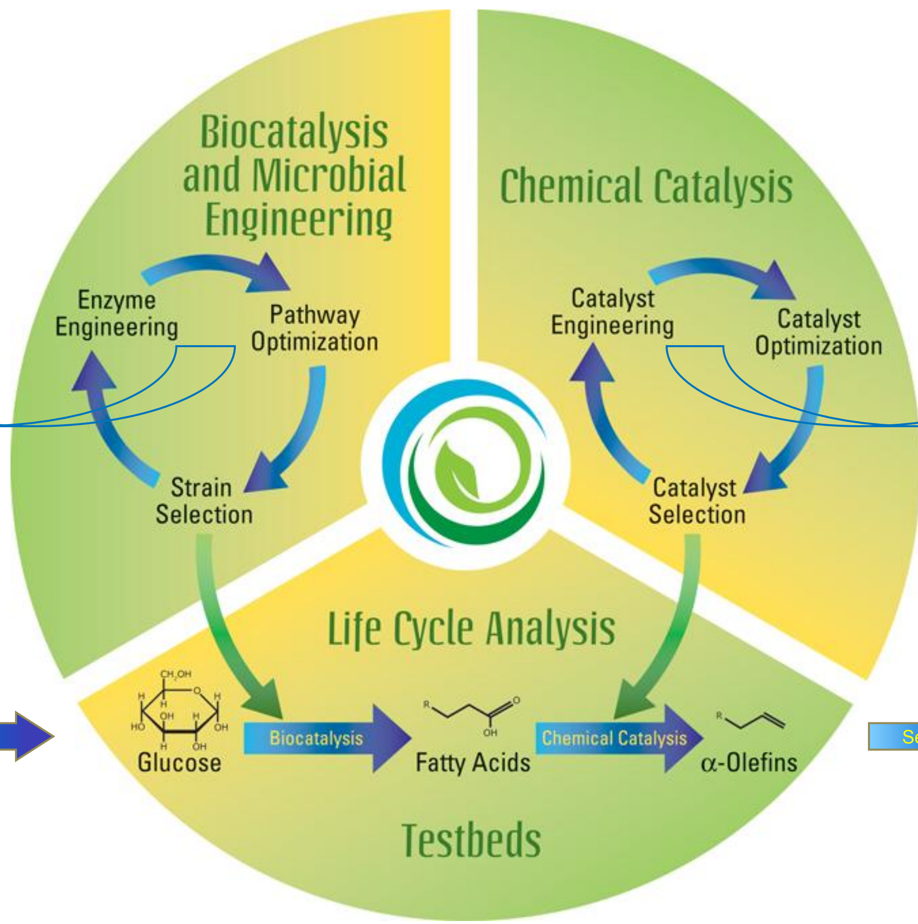
### *Techno-Commercial and Life Cycle Analysis*

***Rob Anex (UWisc) - Lead***
Raj Raman *(ISU)*

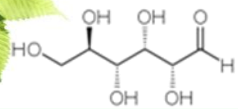
# Overview

*Inventions & Know How in Enzyme and Pathway Engineering*

*Inventions & Know How in Catalyst and Catalysis Engineering*

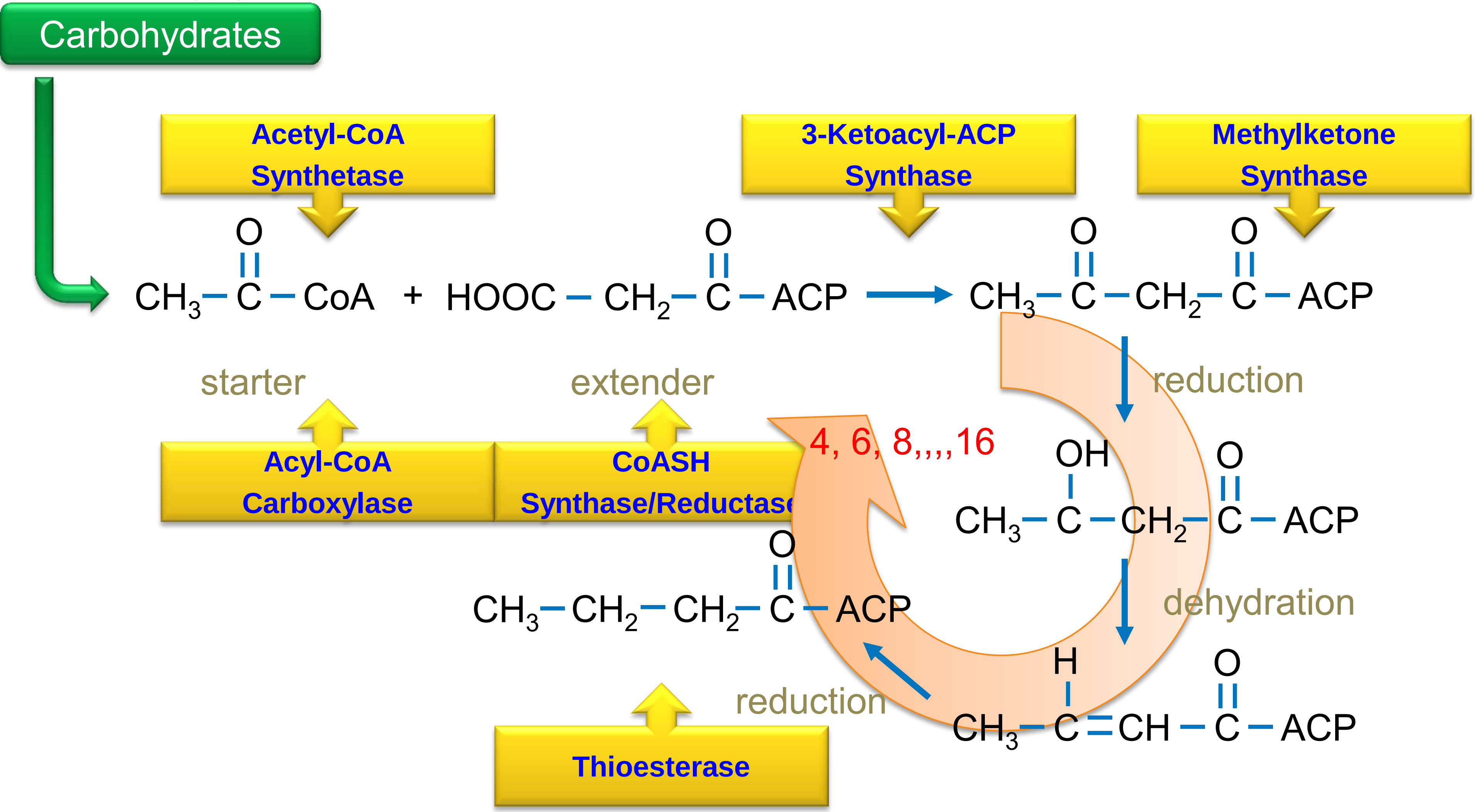



***Biomass Opportunity*** → Processing → … → Separation → ***Biorenewable Chemicals***

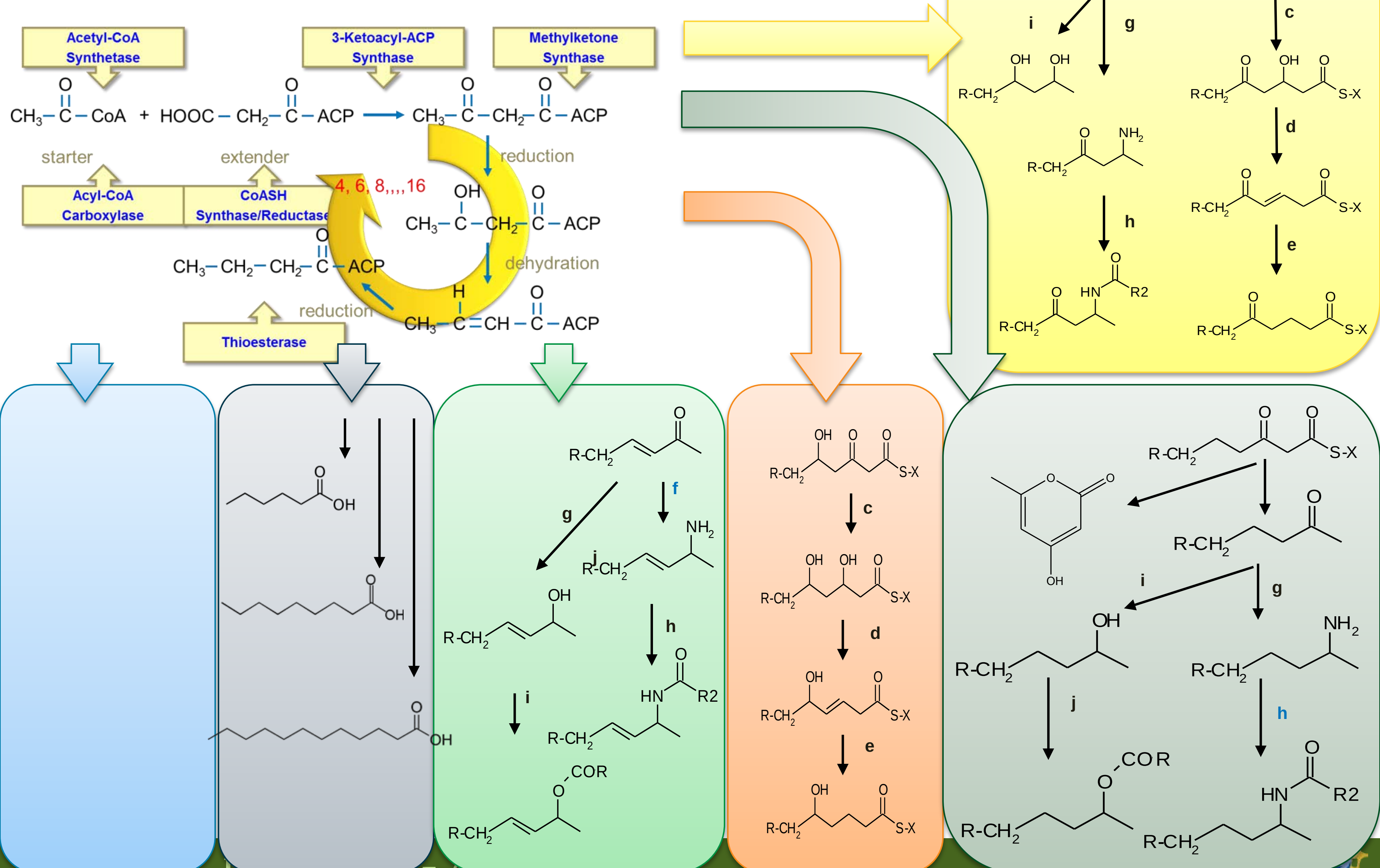


# Metabolism




Carbohydrates
Acetyl-CoA Synthetase
3-Ketoacyl-ACP Synthase
Methylketone Synthase
$CH_3-C(=O)-CoA$ + $HOOC-CH_2-C(=O)-ACP$ → $CH_3-C(=O)-CH_2-C(=O)-ACP$
starter
extender
Acyl-CoA Carboxylase
CoASH Synthase/Reductase
reduction
4, 6, 8,,,,16
$CH_3-C(OH)-CH_2-C(=O)-ACP$
dehydration
$CH_3-C(H)=CH-C(=O)-ACP$
reduction
$CH_3-CH_2-CH_2-C(=O)-ACP$
Thioesterase

# Metabolic Engine



# Microbial Engineering

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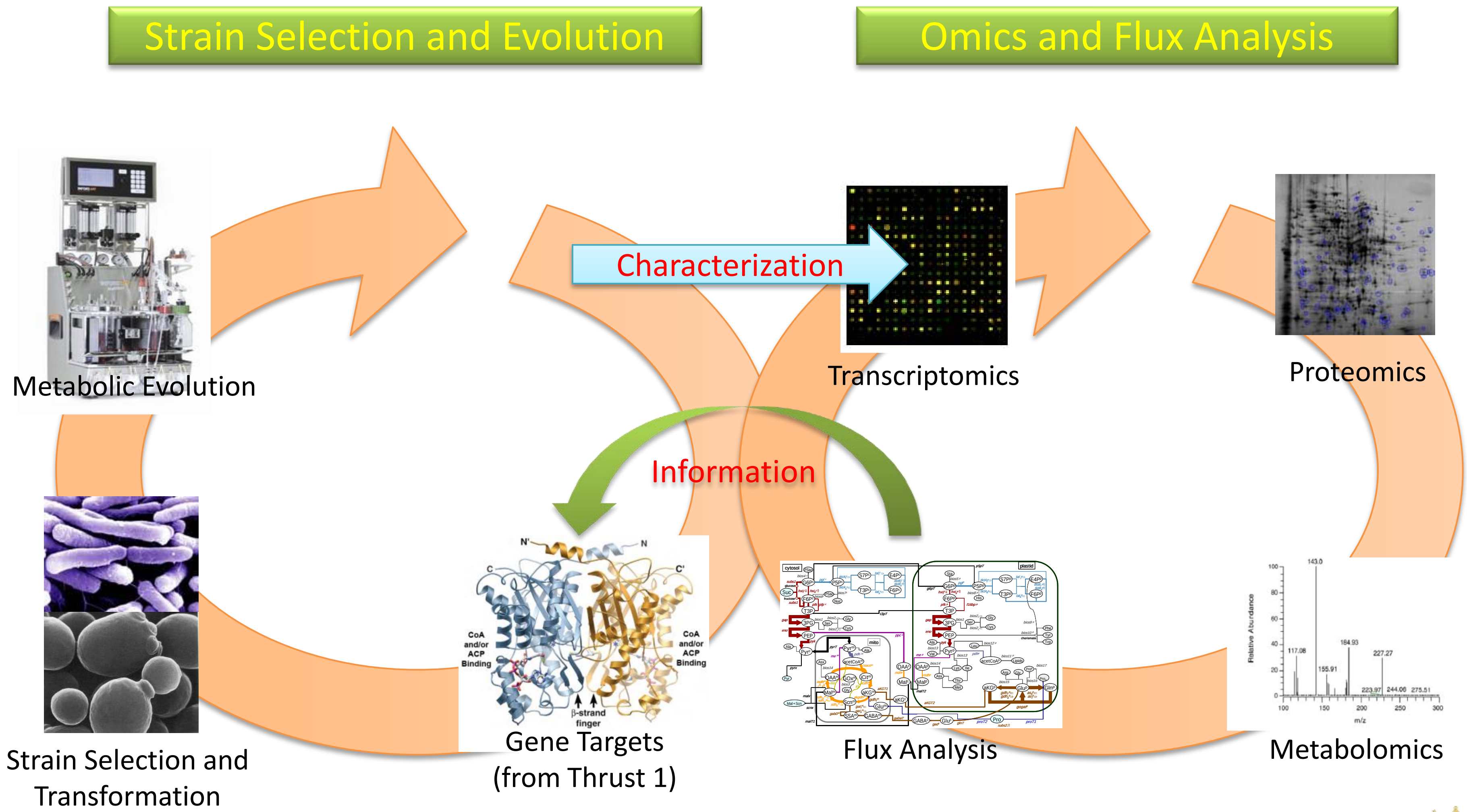


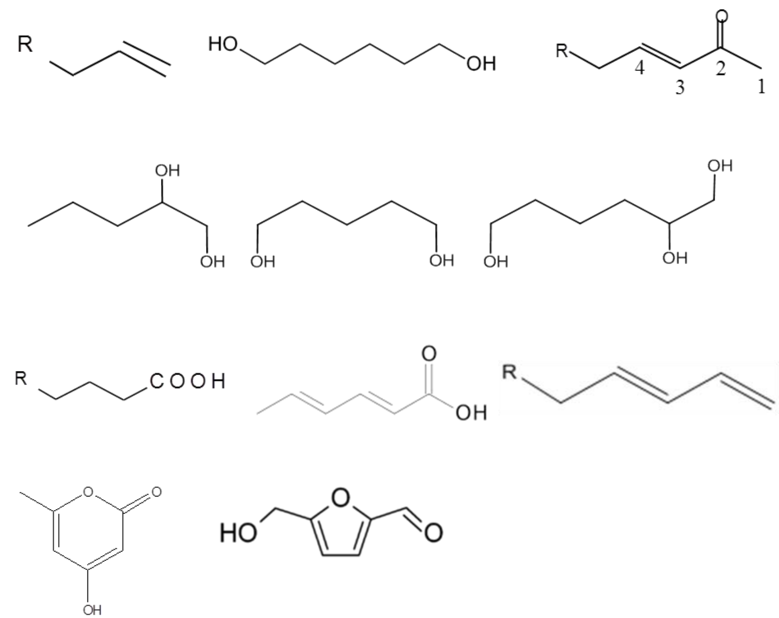
# Chemical Catalysis

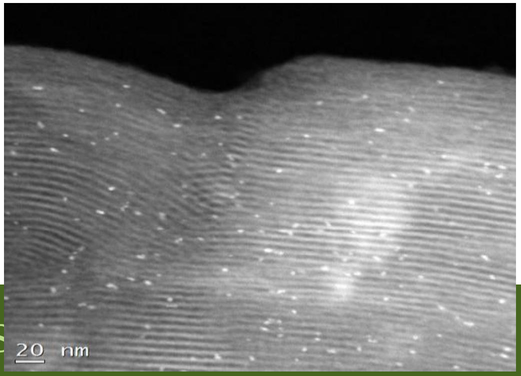
- Hydrogenation, Decarboxylation, Ring opening, Dehydration, Conjugation, Stable catalysts, Catalyst evolution.

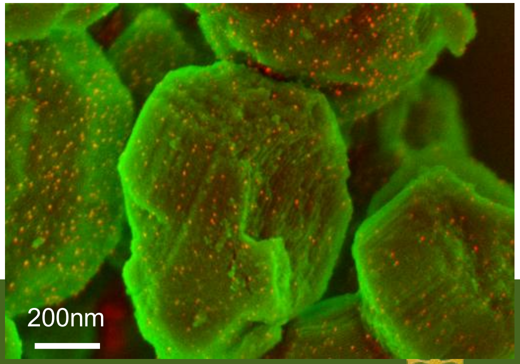
- Significant progress is being made with palladium, platinum and rhodium-based catalysts.

- Hydrothermal stability studies are underway with support systems and catalysts.

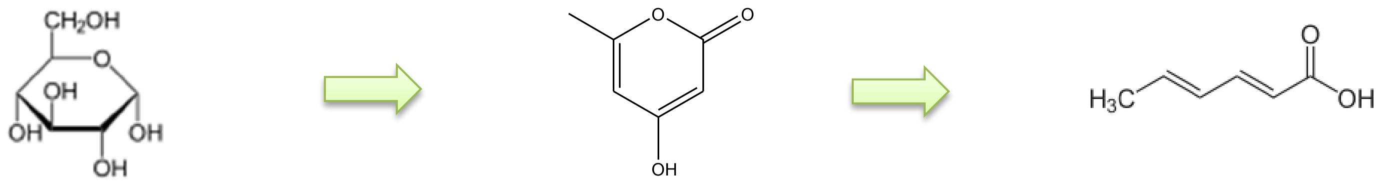
- Catalytic yields are approaching theoretical limits.

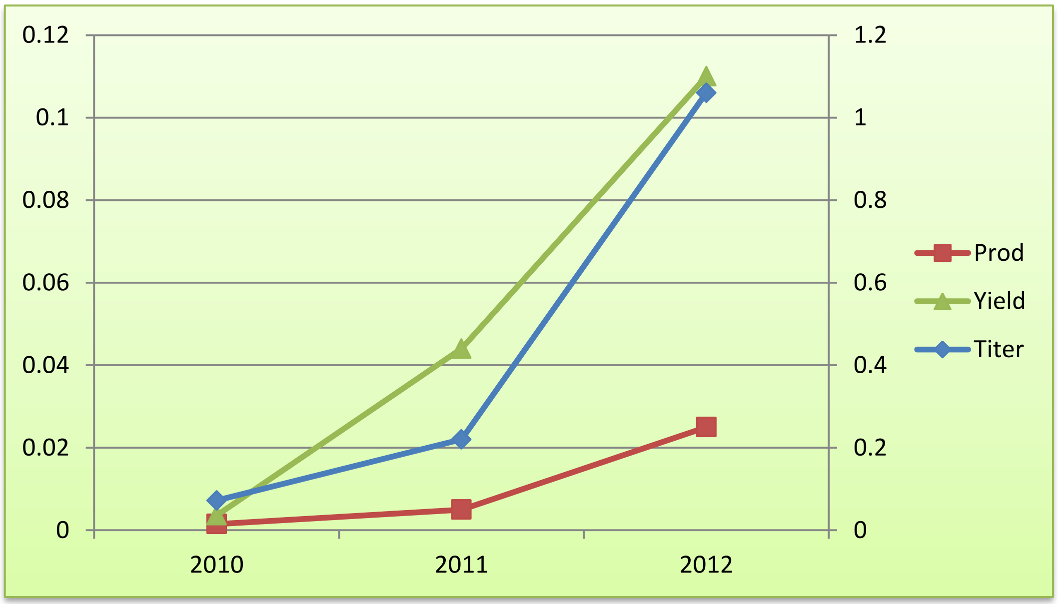




# Progress




| Value | 2010 | 2011 | 2012 |
|---|---|---|---|
| Titer (g/L) | 0.072 | 0.22 | 1.06 |
| Prod. (g/L/h) | 0.0015 | 0.005 | 0.025 |
| $Y_{fer}$ (g/g) % theor. | 0.0036 | 0.044 (9%) | 0.11 (23%) |
| $Conv_{Hydt}$(%) | NA* | 58 | 65** |
| $Sel_{Hydt}$(%) | NA* | 51 | >99** |
| $Conv_{Dehyd/RO}$ (%) | NA* | ~70 | ~70 |
| $Sel_{Dehyd/RO}$(%) | NA* | ~80 | ~80 |

Saccharification

Fermentation

Separation

Catalysis

Purification

# Bio-Based Chemicals Future

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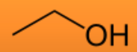
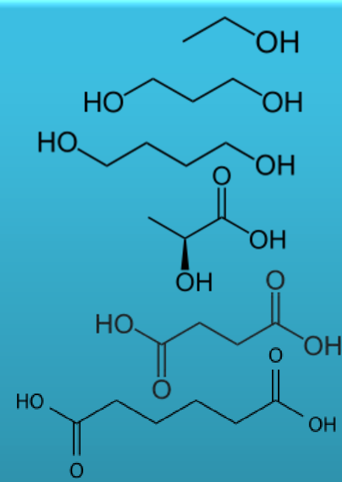
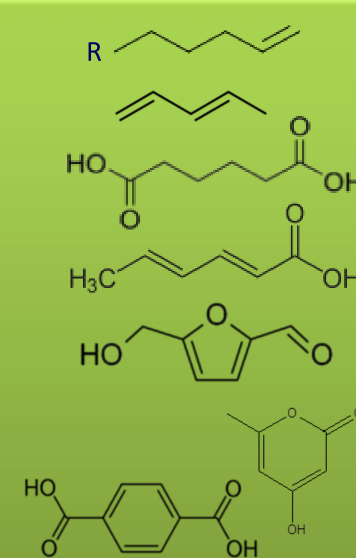
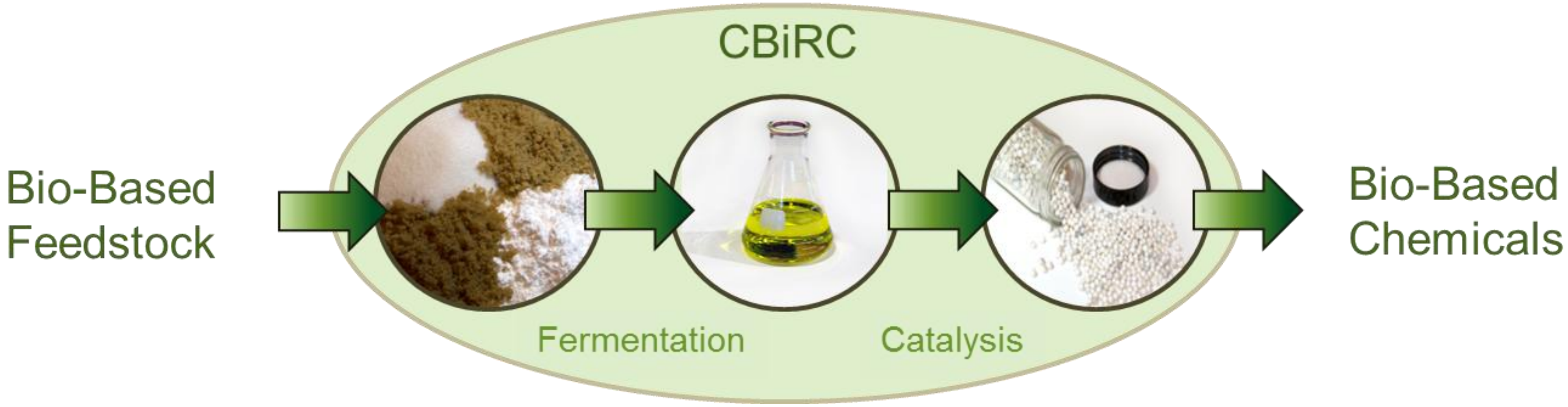
| Ancient | Current | Future |
|---|---|---|
| Ethanol | Ethanol (cel)<br>Propanediol<br>Butanediol<br>Lactic Acid<br>Succinic Acid<br>Adipic Acid | Olefins<br>Dienes<br>Diacids<br>Bifunctionals<br>Rings<br>Aromatics |



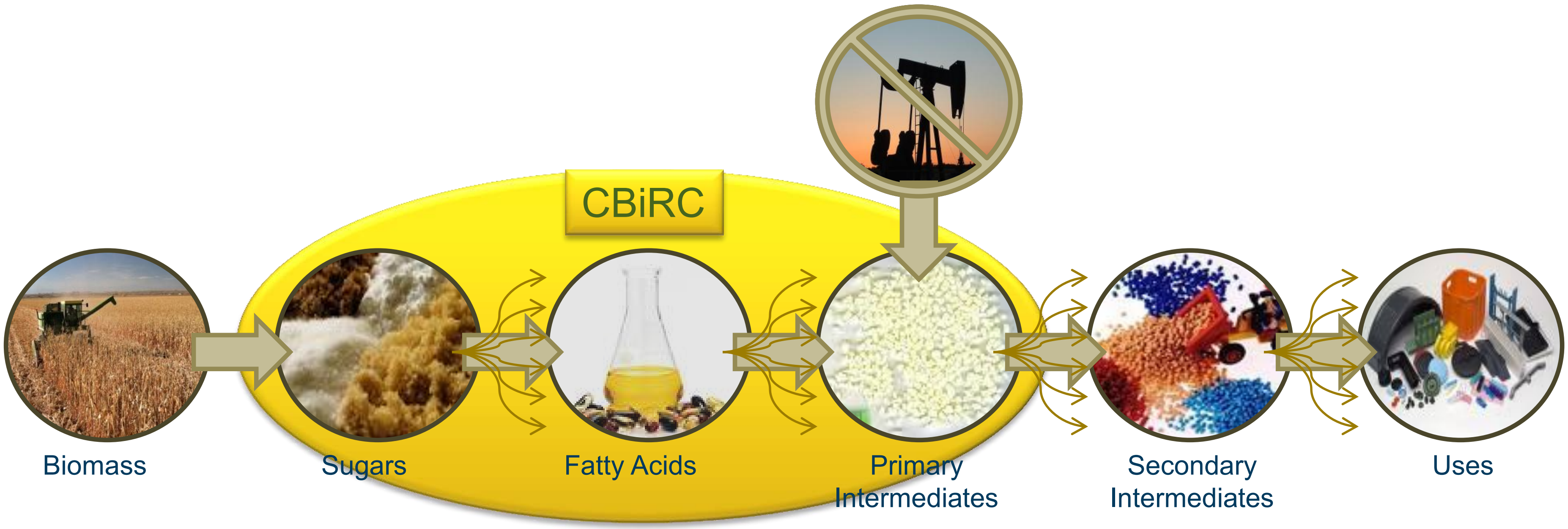



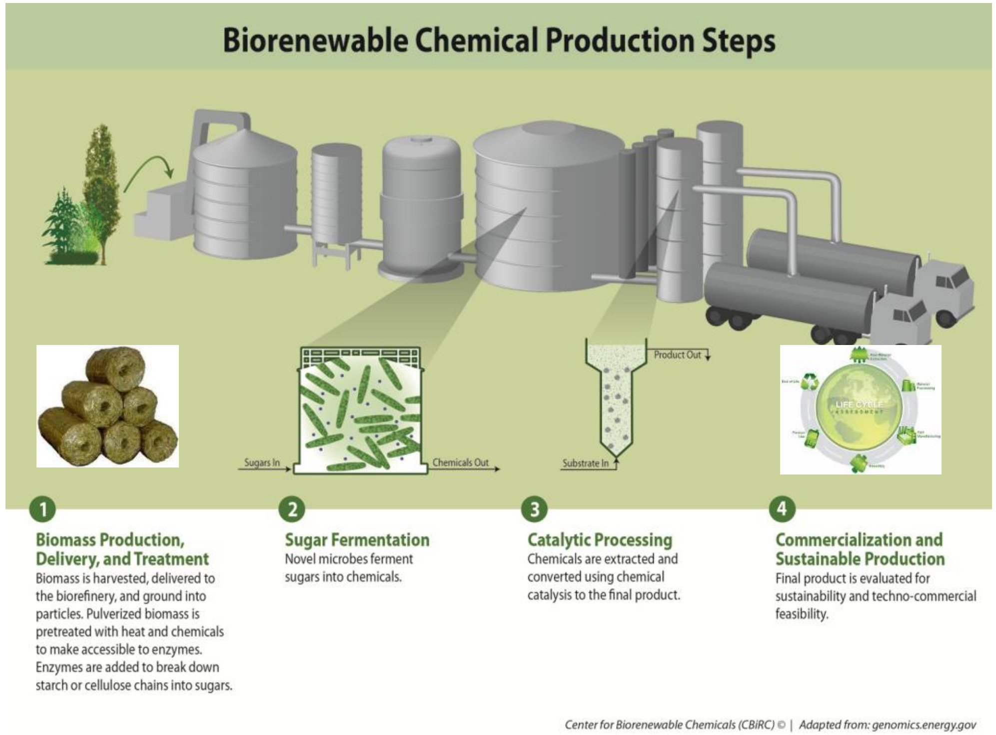
# THANK YOU!!


CBiRC
Bio-Based
Feedstock
Fermentation
Catalysis
Bio-Based
Chemicals

# Value Chain


CBiRC
Biomass
Sugars
Fatty Acids
Primary Intermediates
Secondary Intermediates
Uses

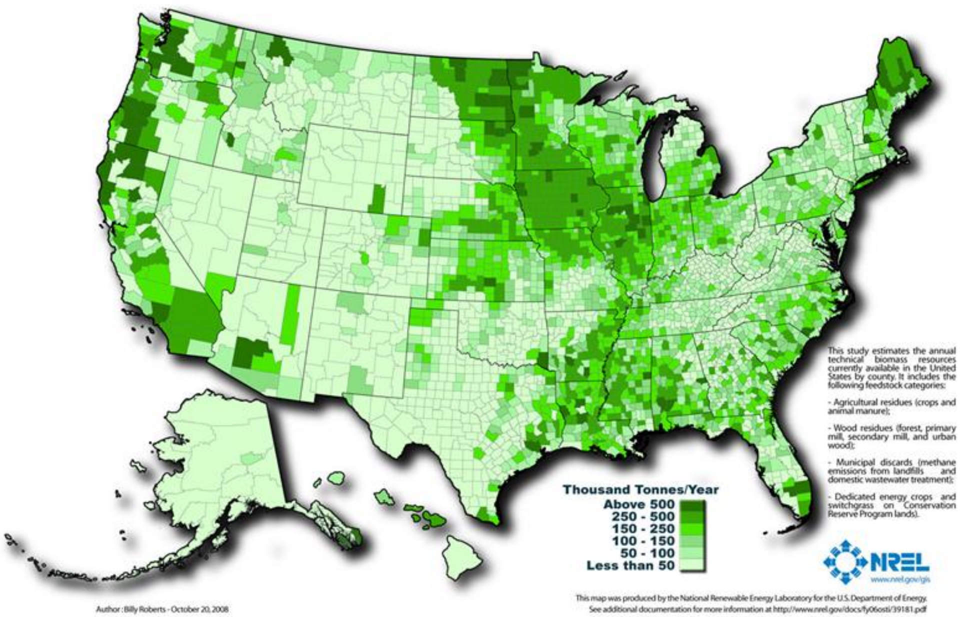
# Implementation



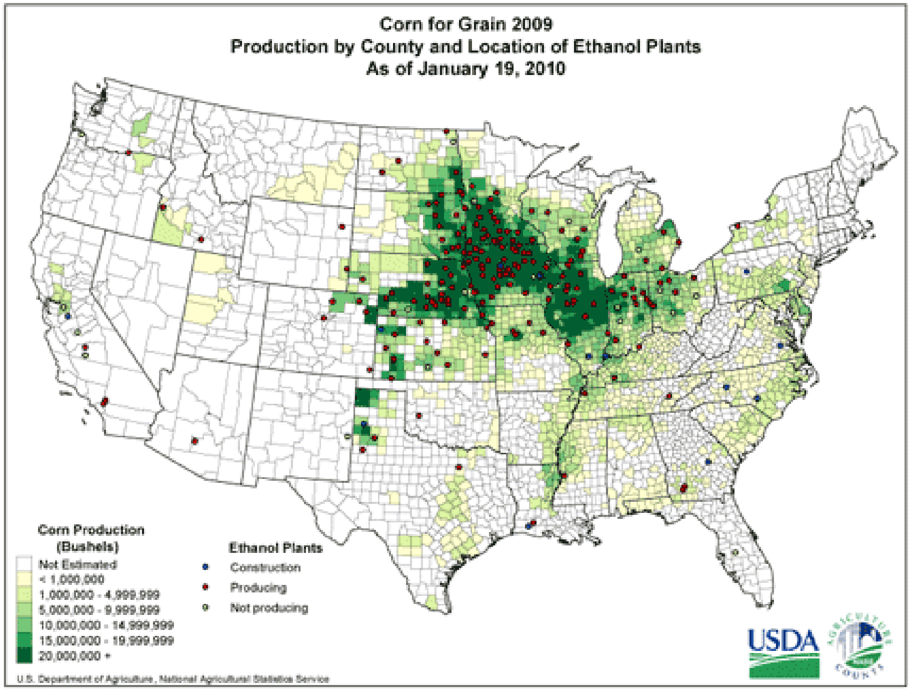

Testbeds (1L) → Pre-Pilot (250L) → Pilot (5,000L) → Plant (T) → Iowa (10mT/yr)

mg/batch 1-10g 1-2kg 20-40kg 1,000Tonnes 100,000T

# Iowa



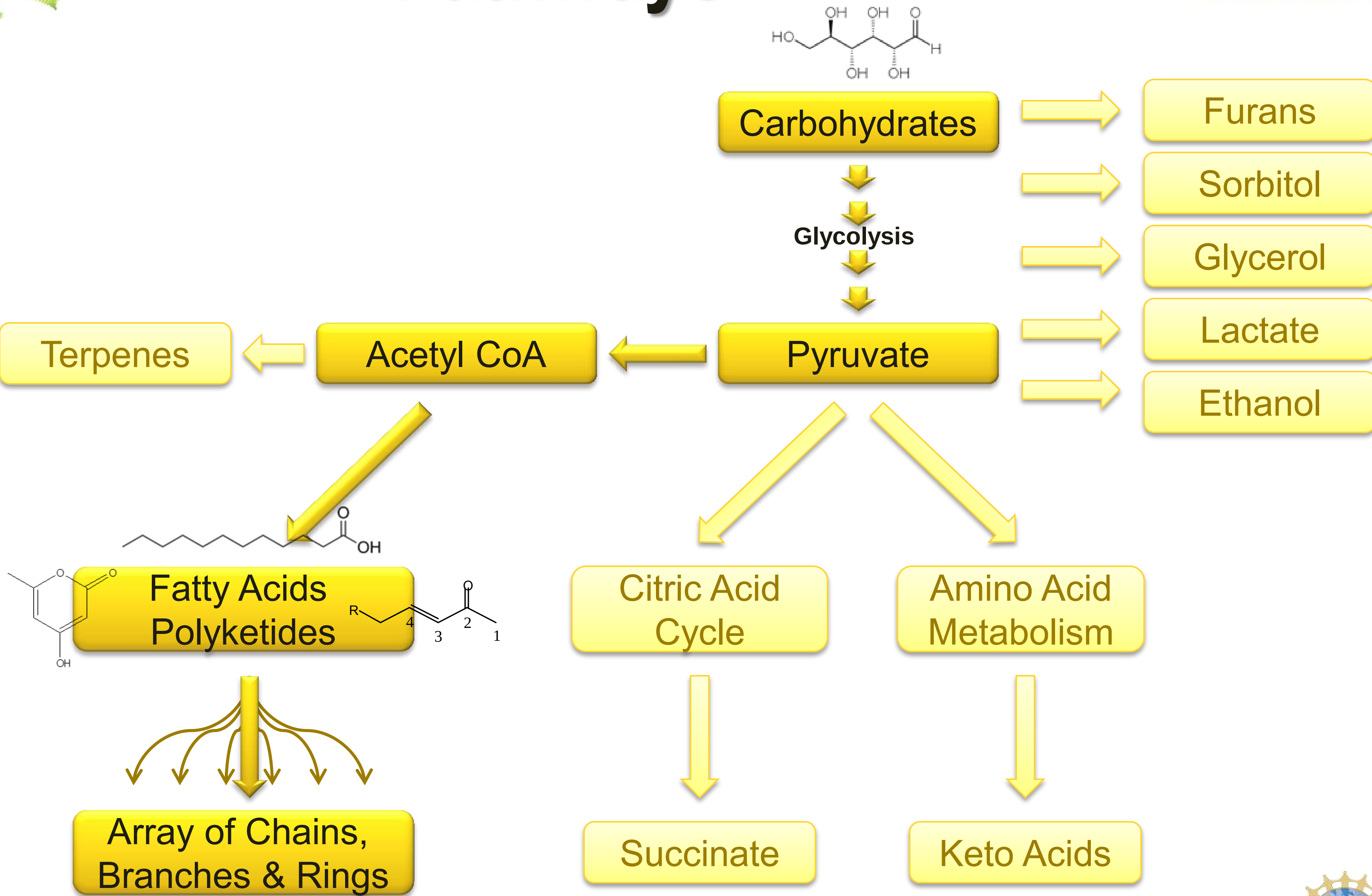
Thousand Tonnes/Year
Above 500
250 - 500
150 - 250
100 - 150
50 - 100
Less than 50
This study estimates the annual technical biomass resources currently available in the United States by county. It includes the following feedstock categories:
- Agricultural residues (crops and animal manure);
- Wood residues (forest, primary mill, secondary mill, and urban wood);
- Municipal discards (methane emissions from landfills and domestic wastewater treatment);
- Dedicated energy crops and switchgrass on Conservation Reserve Program lands).
NREL
www.nrel.gov/gis
This map was produced by the National Renewable Energy Laboratory for the U.S. Department of Energy.
See additional documentation for more information at http://www.nrel.gov/docs/fy06osti/39181.pdf
Author : Billy Roberts - October 20, 2008

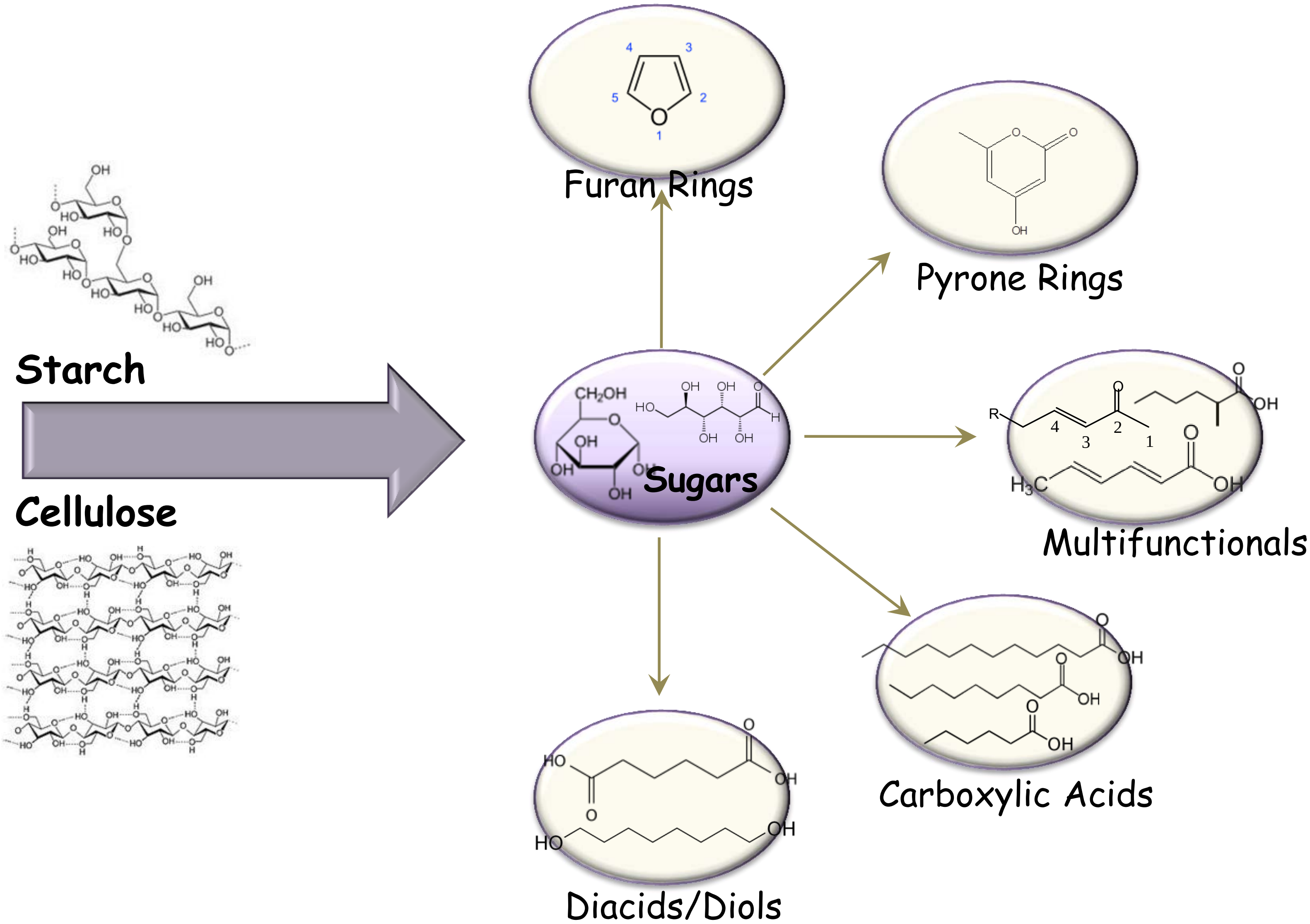
Corn for Grain 2009
Production by County and Location of Ethanol Plants
As of January 19, 2010
Corn Production (Bushels)
Not Estimated
< 1,000,000
1,000,000 - 4,999,999
5,000,000 - 9,999,999
10,000,000 - 14,999,999
15,000,000 - 19,999,999
20,000,000 +
Ethanol Plants
Construction
Producing
Not producing
USDA
U.S. Department of Agriculture, National Agricultural Statistics Service

# Pathways




HO
OH
OH
O
H
OH
OH
Carbohydrates
Glycolysis
Furans
Sorbitol
Glycerol
Lactate
Ethanol
Terpenes
Acetyl CoA
Pyruvate
O
OH
O
O
Fatty Acids
Polyketides
OH
R
O
4
3
2
1
Citric Acid
Cycle
Amino Acid
Metabolism
Array of Chains,
Branches & Rings
Succinate
Keto Acids

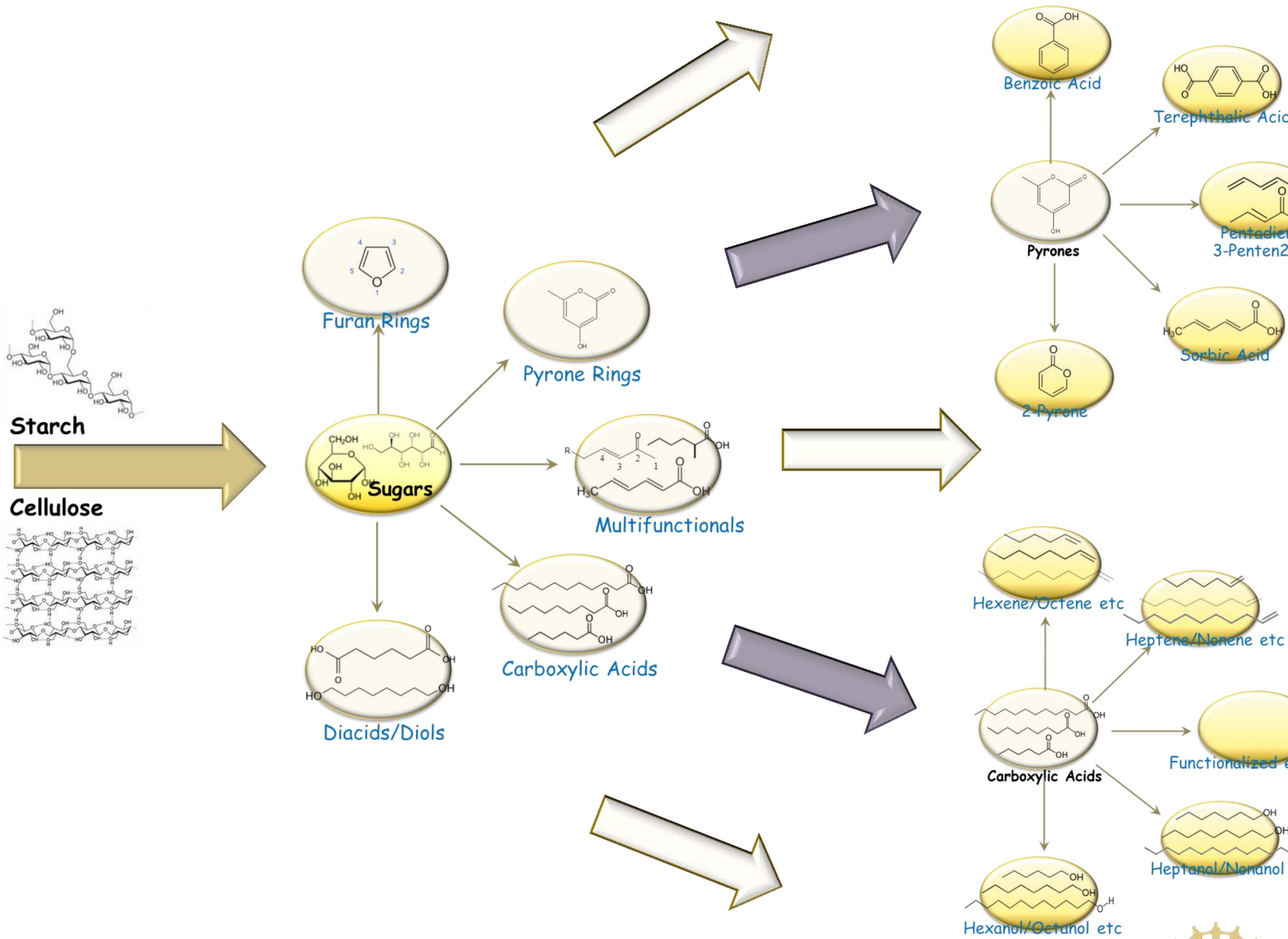
# Vision



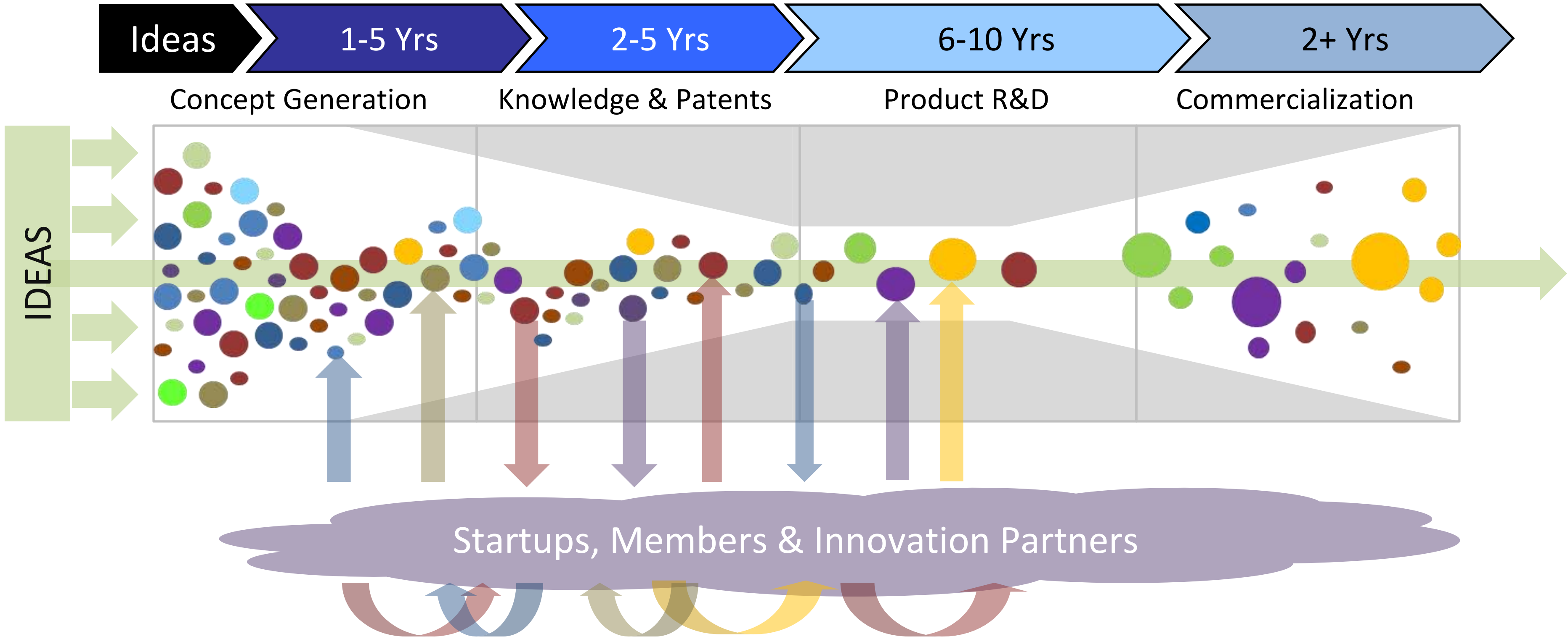
Furan Rings
Pyrone Rings
Starch
Sugars
Multifunctionals
Cellulose
Carboxylic Acids
Diacids/Diols

# Vision

NSF Engineering Research Center for Biorenewable Chemicals



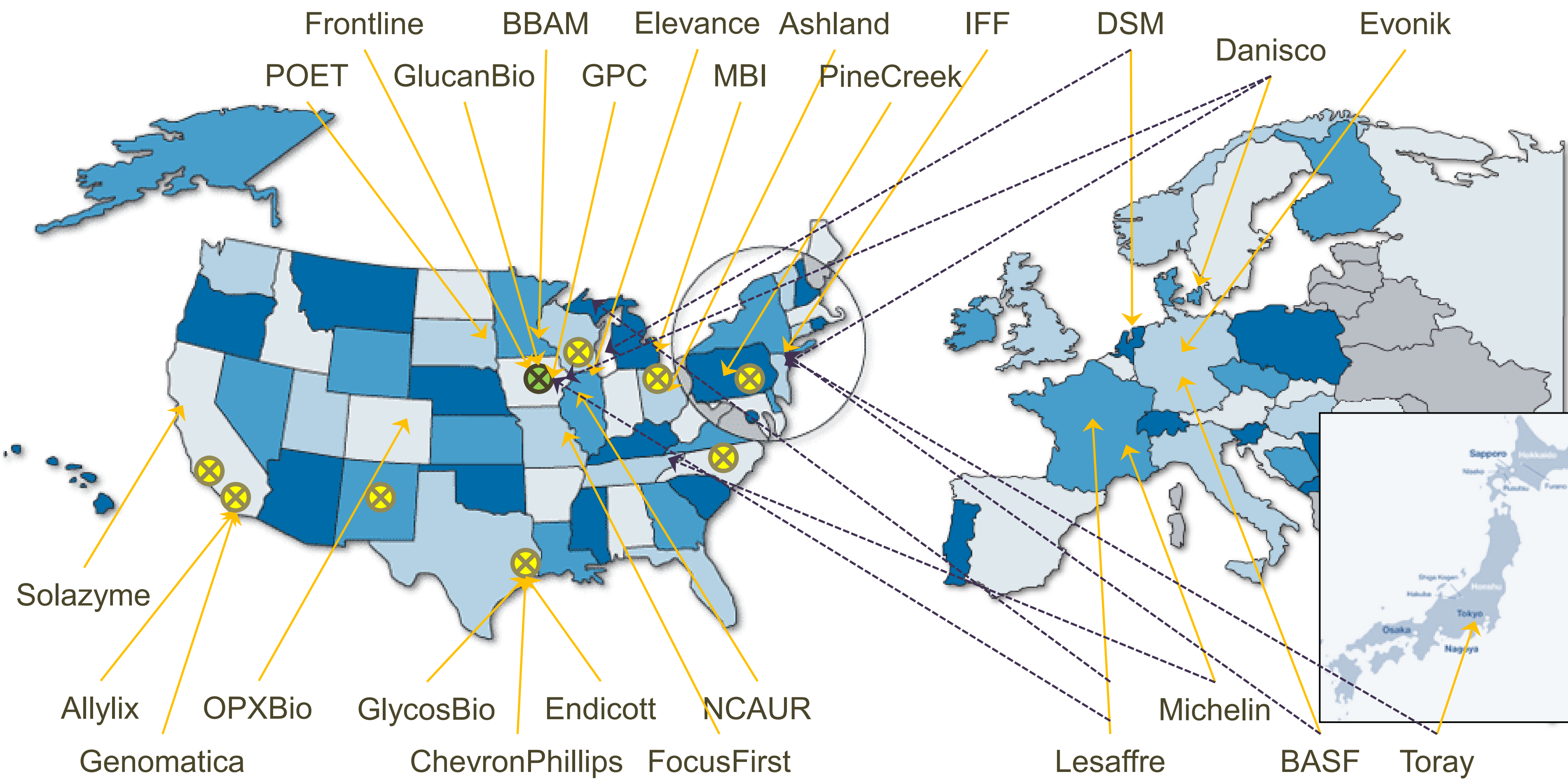
# Innovation



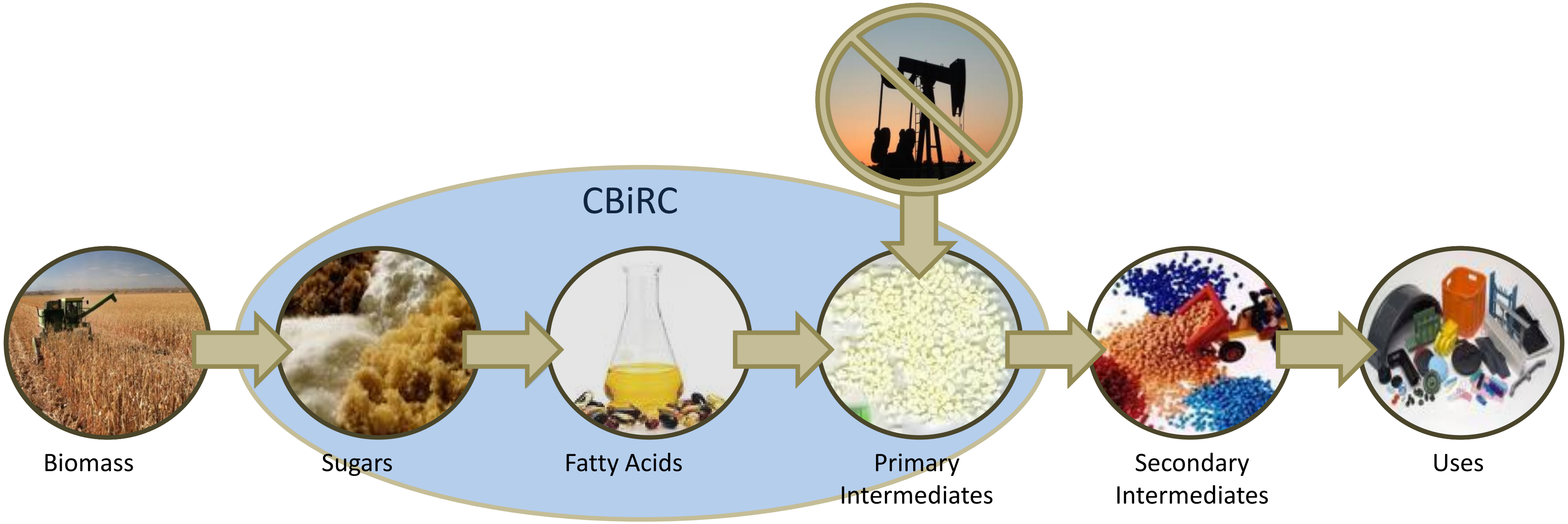

A de-risking technology for translational research.

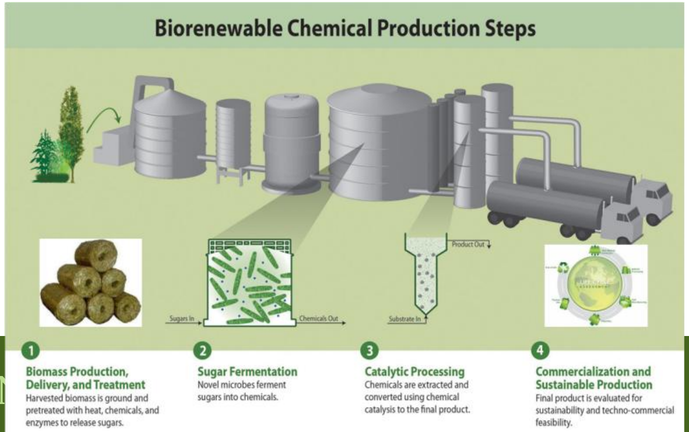
# Partnerships

CBiRC
NSF Engineering Research
Center for Biorenewable Chemicals



# Making Biobased Chemicals



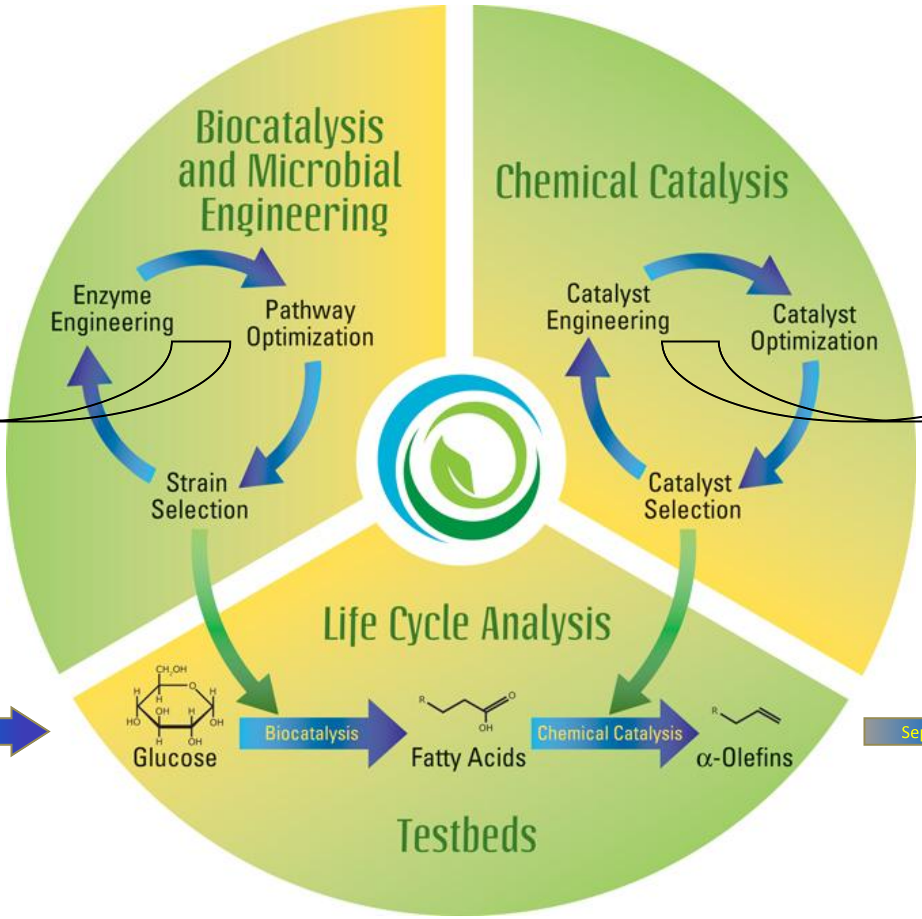




# Research

CBiRC
NSF Engineering Research Center for Biorenewable Chemicals

*Inventions & Know How in Enzyme and Pathway Engineering*

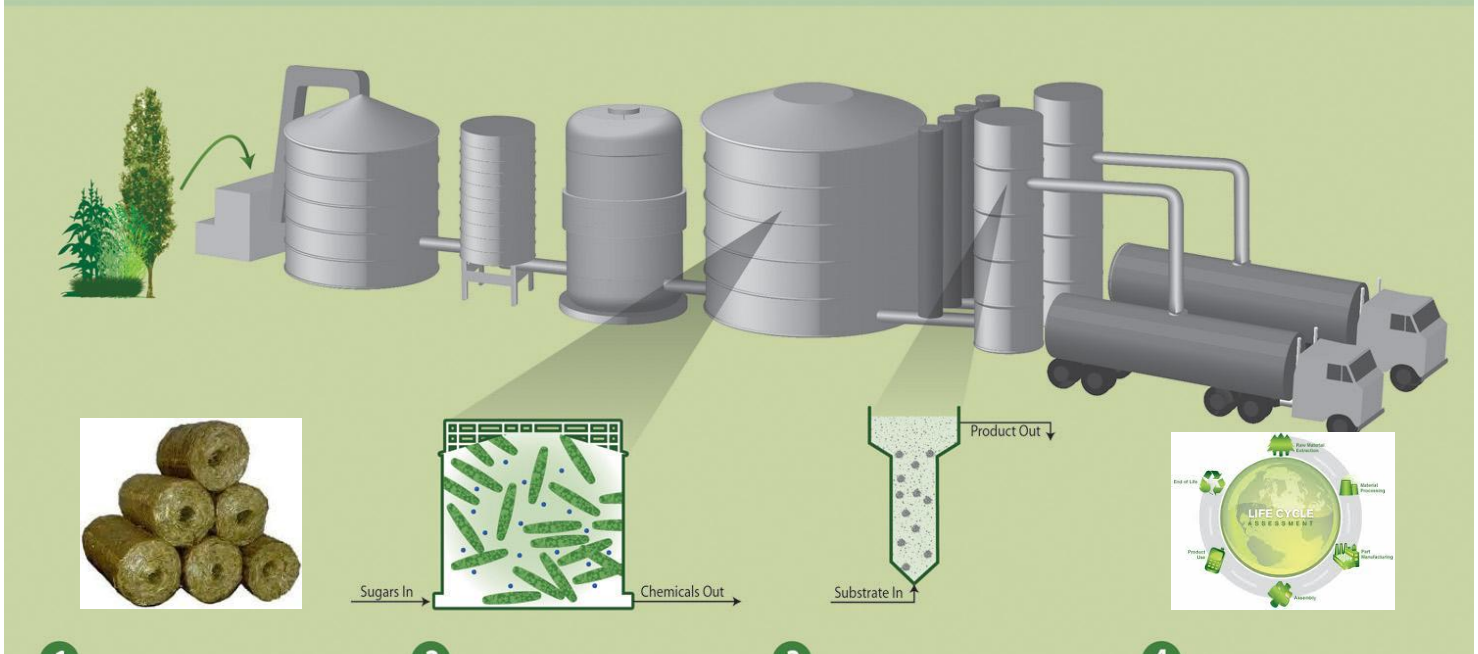
*Inventions & Know How in Catalyst and Catalysis Engineering*




***Biomass Opportunity*** → Processing → Separation → ***Biorenewable Chemicals***

# Future

## Biorenewable Chemical Production Steps




**1 Biomass Production, Delivery, and Treatment**
Harvested biomass is ground and pretreated with heat, chemicals, and enzymes to release sugars.

**2 Sugar Fermentation**
Novel microbes ferment sugars into chemicals.

**3 Catalytic Processing**
Chemicals are extracted and converted using chemical catalysis to the final product.

**4 Commercialization and Sustainable Production**
Final product is evaluated for sustainability and techno-commercial feasibility.

*Center for Biorenewable Chemicals (CBiRC) © | Adapted from: genomics.energy.gov*

# NSF Translational Research