Next Generation Hydrocarbon Biorefineries

National Academy Workshop:
Expanding Biofuel Production

Madison, WI

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Catalysis and Biocatalysis Program
Directorate for Engineering
National Science Foundation

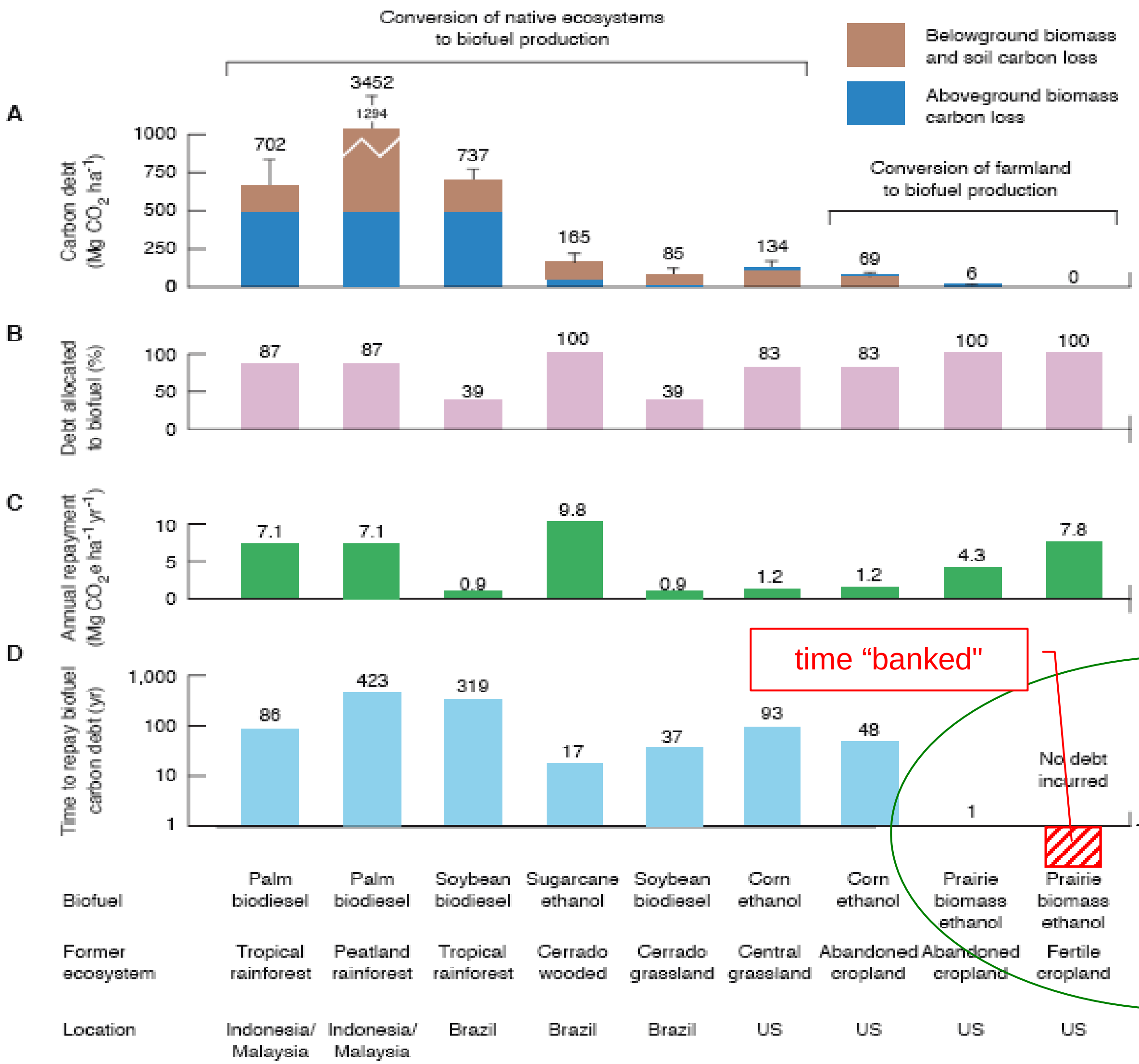
June 23rd, 2009

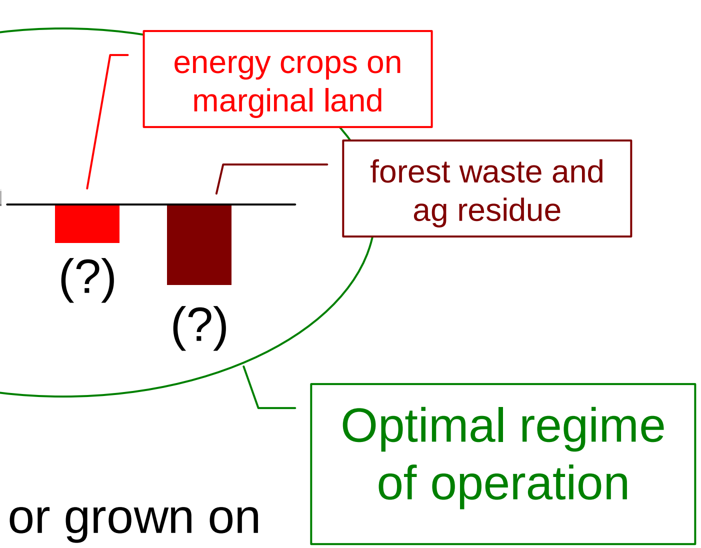
Current Situation in Biofuels

- Energy Independence and Security Act of 2007
  - 36 billion gallons of renewable fuel by 2022
  - 15 billion cap on corn ethanol
  - Increase average gas mileage from 25 to 35 MPG
    - Flex fuel: 25 MPG $\rightarrow$ 18 MPG
    - Renewable fuels must be exempted from CAFE increase

Challenge 1:
How to produce a renewable biofuel without incurring a loss in gas mileage.

Avoidance of Land Use Change Penalty





- Use fallow/abandoned farmland and marginal land with high debt-paying energy crops:
  - Lignocellulose:
    - Switchgrass
    - Sorghum
- Avoid land use change altogether:
  - Forest waste
  - Agricultural residue

Fargione et al: "biofuels made from waste biomass… or grown on abandoned… lands planted with perennials incur little or no carbon debt…

Challenge for Biofuels:

- Mass produce a renewable biofuel which incurs penalties in neither gas mileage or lifecycle greenhouse gas emissions.
- Utilization of existing fuel infrastructure (pipelines, refineries, engines) would be advantageous

The Solution:

- Produce hydrocarbons from lignocellulose grown with minimal land use change

Challenge for Biofuels:

- Mass produce a renewable biofuel which incurs penalties in neither gas mileage or lifecycle greenhouse gas emissions.
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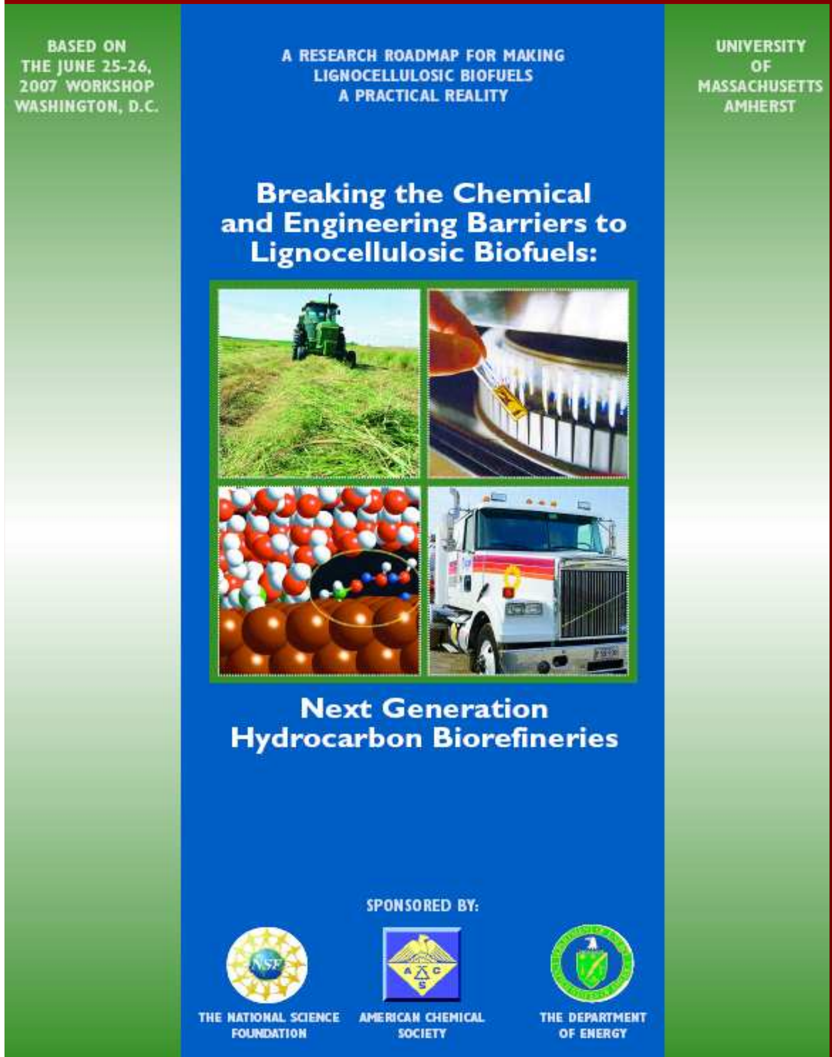
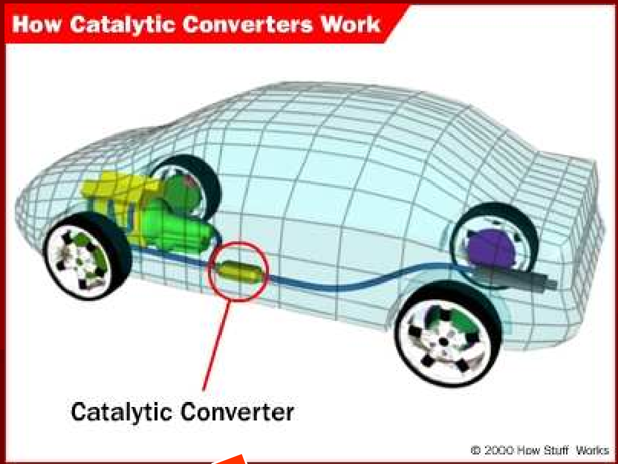
Roadmap for Hydrocarbon Production

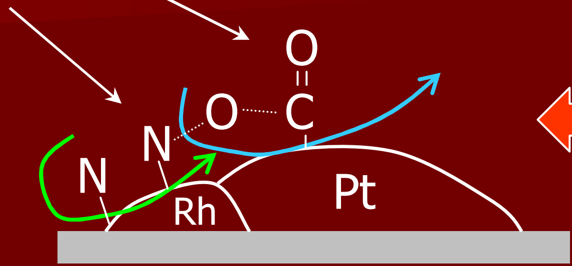


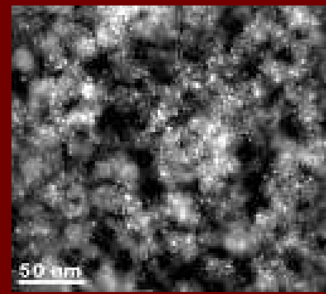
- 2007 NSF/ENG and DOE/EERE Cosponsored Workshop in June, 2007
- Workshop participants:
  - 71 invited participants
  - 27 academics from 24 universities
  - 19 companies, small and large
  - 13 representatives from 5 national labs
  - 10 program managers (NSF, DOE, USDA)
- Workshops Goals:
  - Articulate the role of chemistry and catalysis in the mass production of green gasoline, diesel and jet fuel from lignocellulose.
  - Understand the key chemical and engineering challenges.
  - Develop a roadmap for the mass production of next generation hydrocarbon biofuels.
- Final Report Released April 1, 2008
  - www.ecs.umass.edu/biofuels/roadmap.htm
- Input for Interagency Working Group on Biomass Conversion

The Catalyst: Heart of a Catalytic Converter

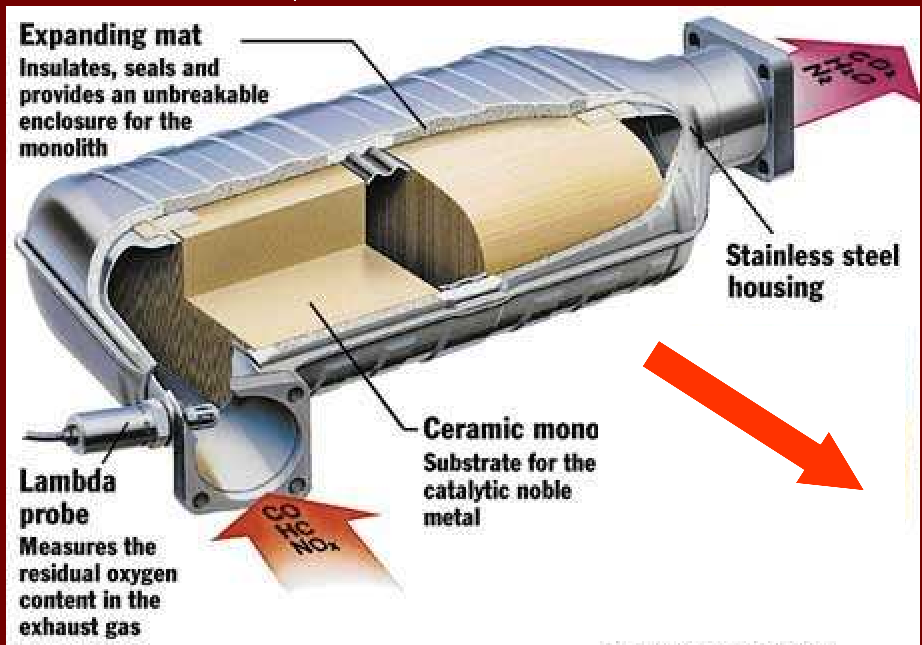


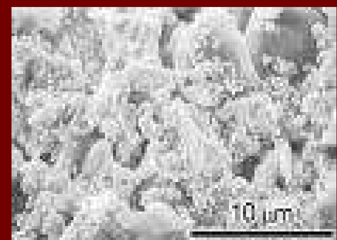
$NO + CO \rightarrow N_2 + CO_2$



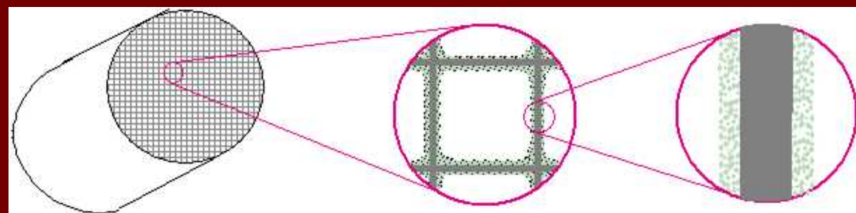


$Pt/Rh/Al_2O_3$ catalyst

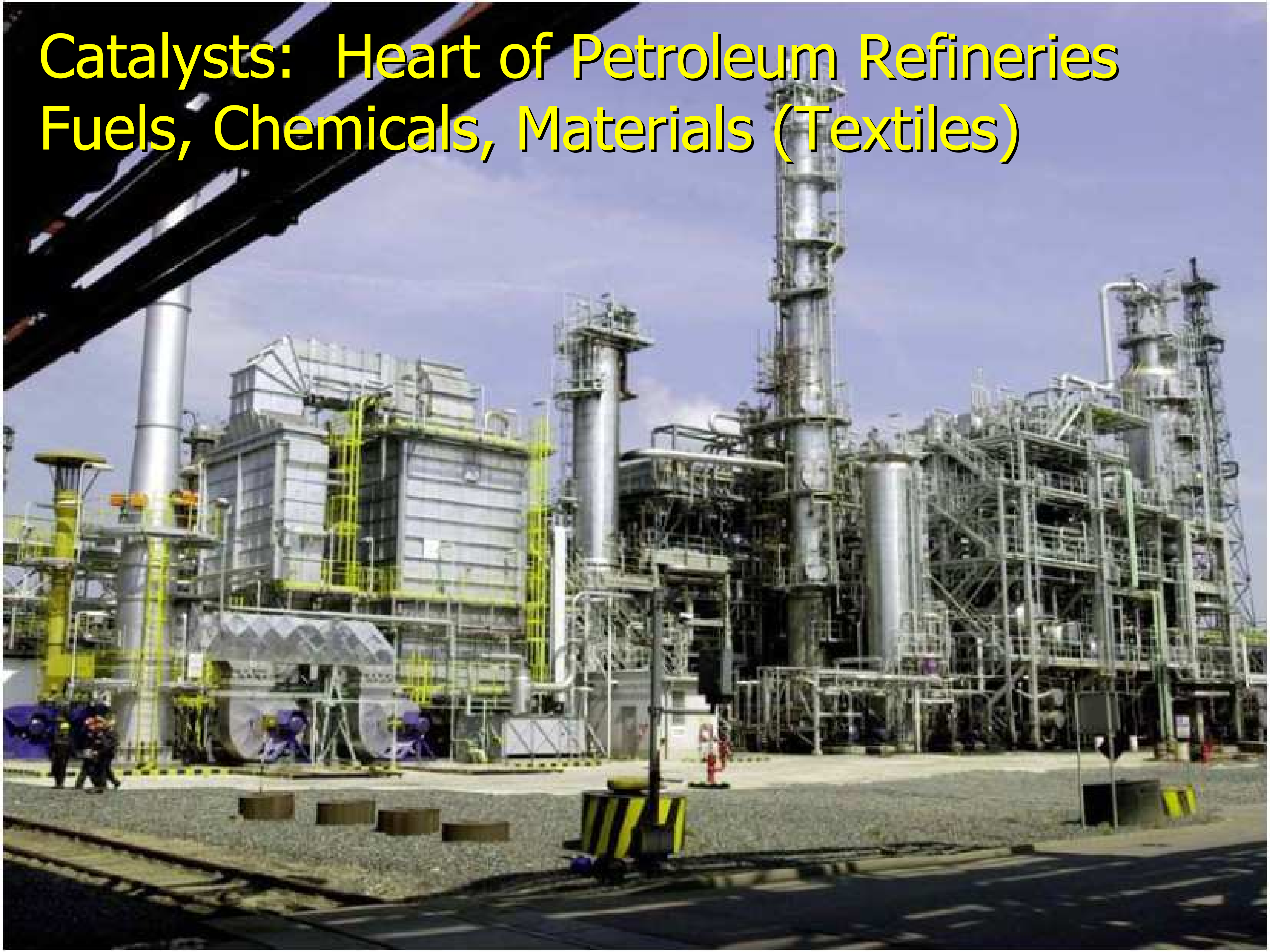


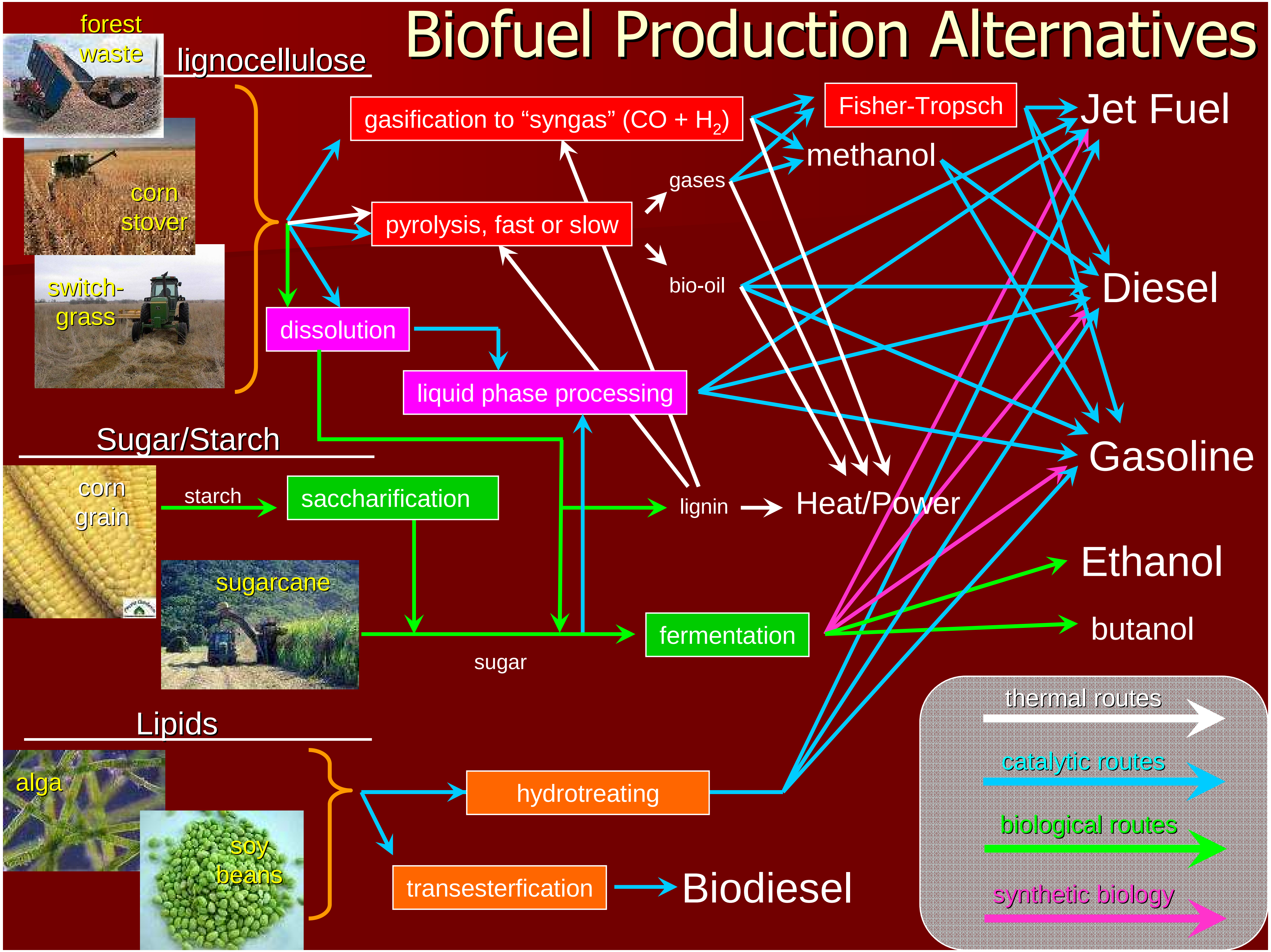


washcoat



Catalysts: Heart of Petroleum Refineries
Fuels, Chemicals, Materials (Textiles)

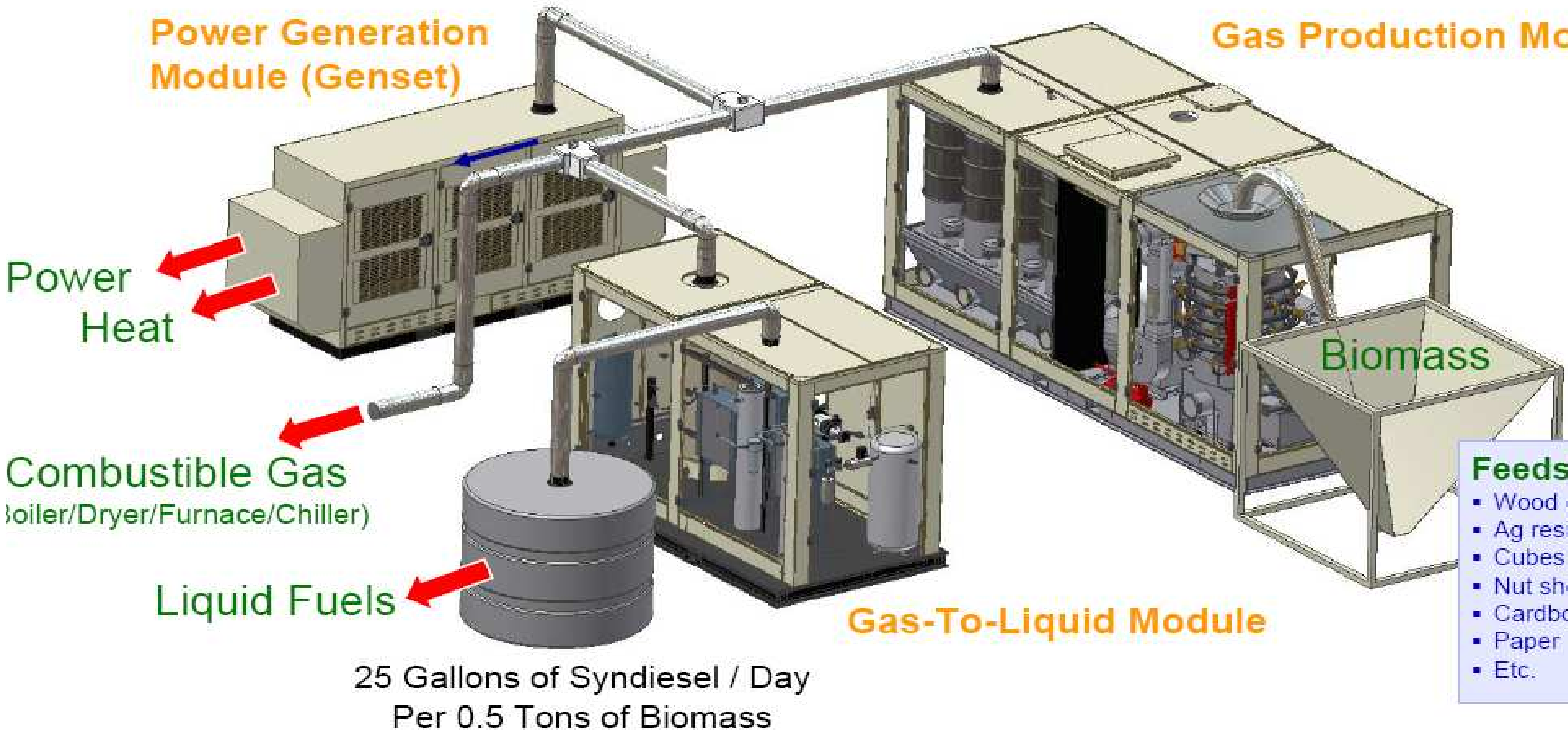




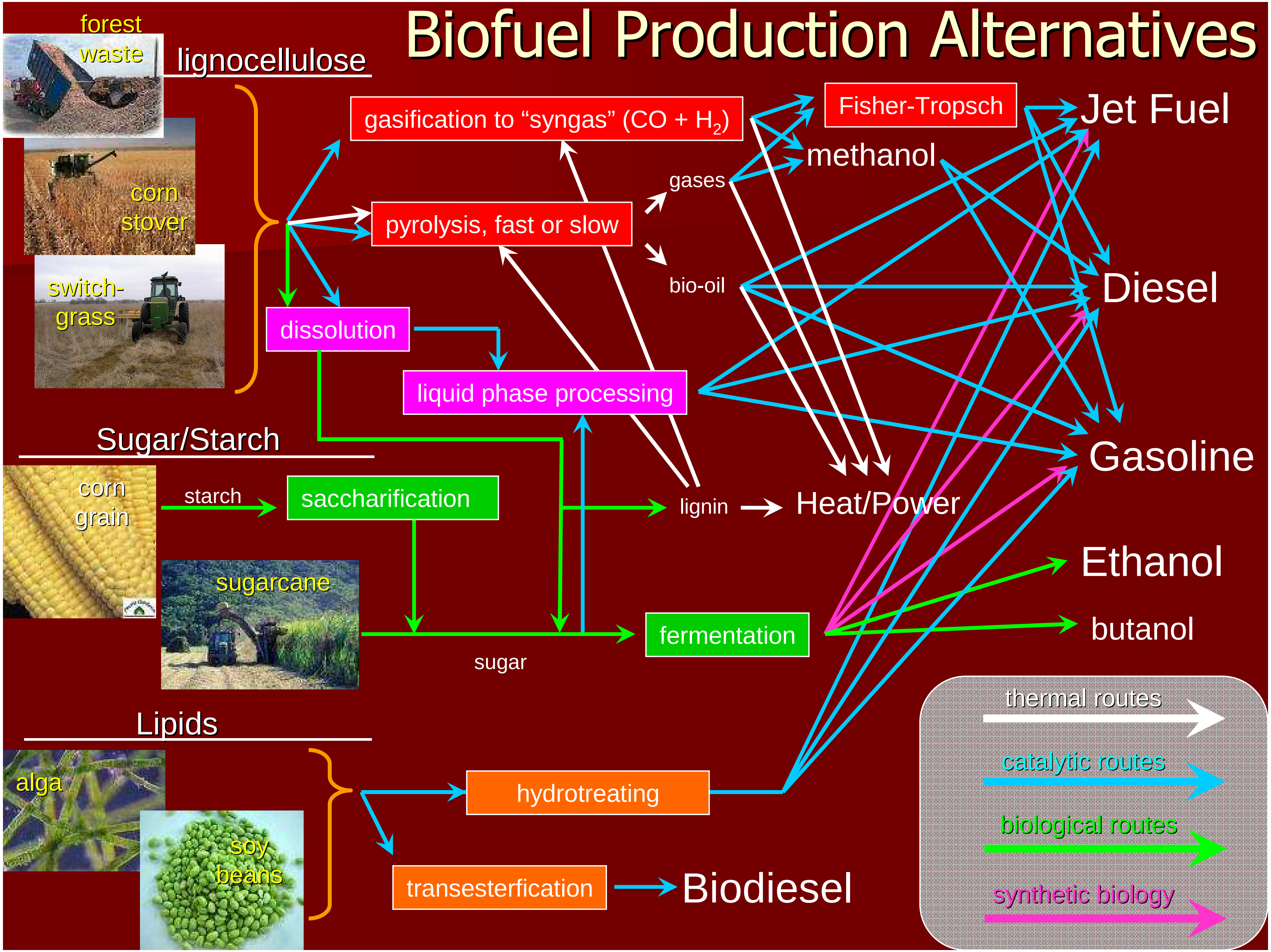
Biofuel Production Alternatives
forest waste
lignocellulose
corn stover
switch-grass
gasification to “syngas” (CO + H2)
pyrolysis, fast or slow
dissolution
liquid phase processing
gases
bio-oil
Fisher-Tropsch
methanol
Jet Fuel
Diesel
Gasoline
Sugar/Starch
corn grain
starch
saccharification
sugarcane
sugar
fermentation
lignin
Heat/Power
Ethanol
butanol
Lipids
alga
soy beans
hydrotreating
transesterfication
Biodiesel
thermal routes
catalytic routes
biological routes
synthetic biology

BioMax – Independent Energy Solution

On-site Electricity, Heat, and Synthetic Liquid Fuels from Biomass



Feedstocks:
- Wood chips
- Ag residues
- Cubes & Pellets
- Nut shells
- Cardboard
- Paper
- Etc.



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Ethanol
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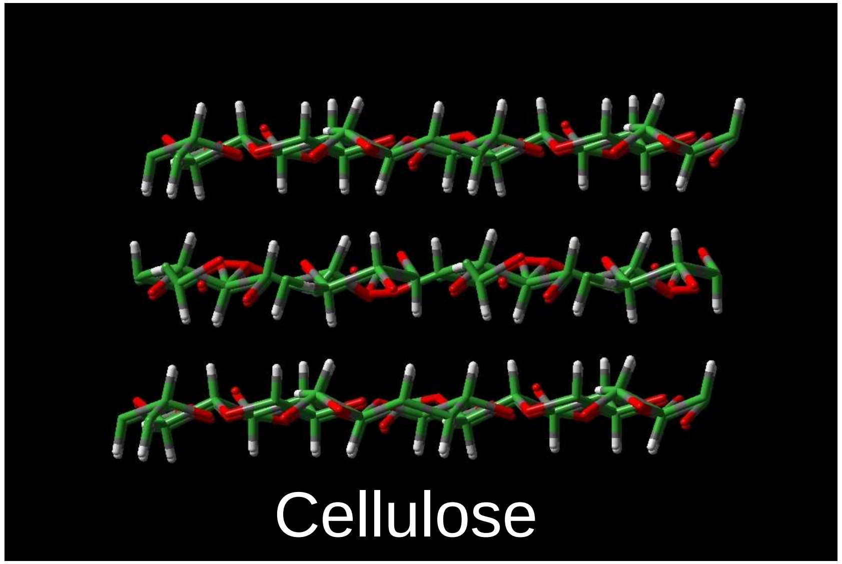
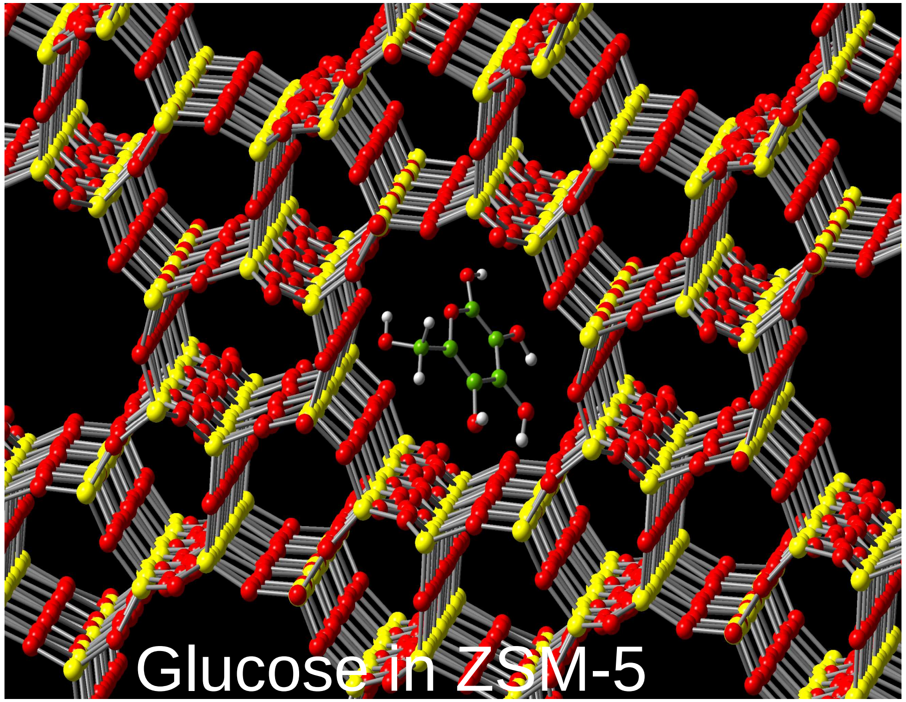
Lipids
alga
soy beans
hydrotreating
transesterfication
Biodiesel
thermal routes
catalytic routes
biological routes
synthetic biology

Gasoline from Cellulose by Catalytic Fast Pyrolysis in a Single Reactor



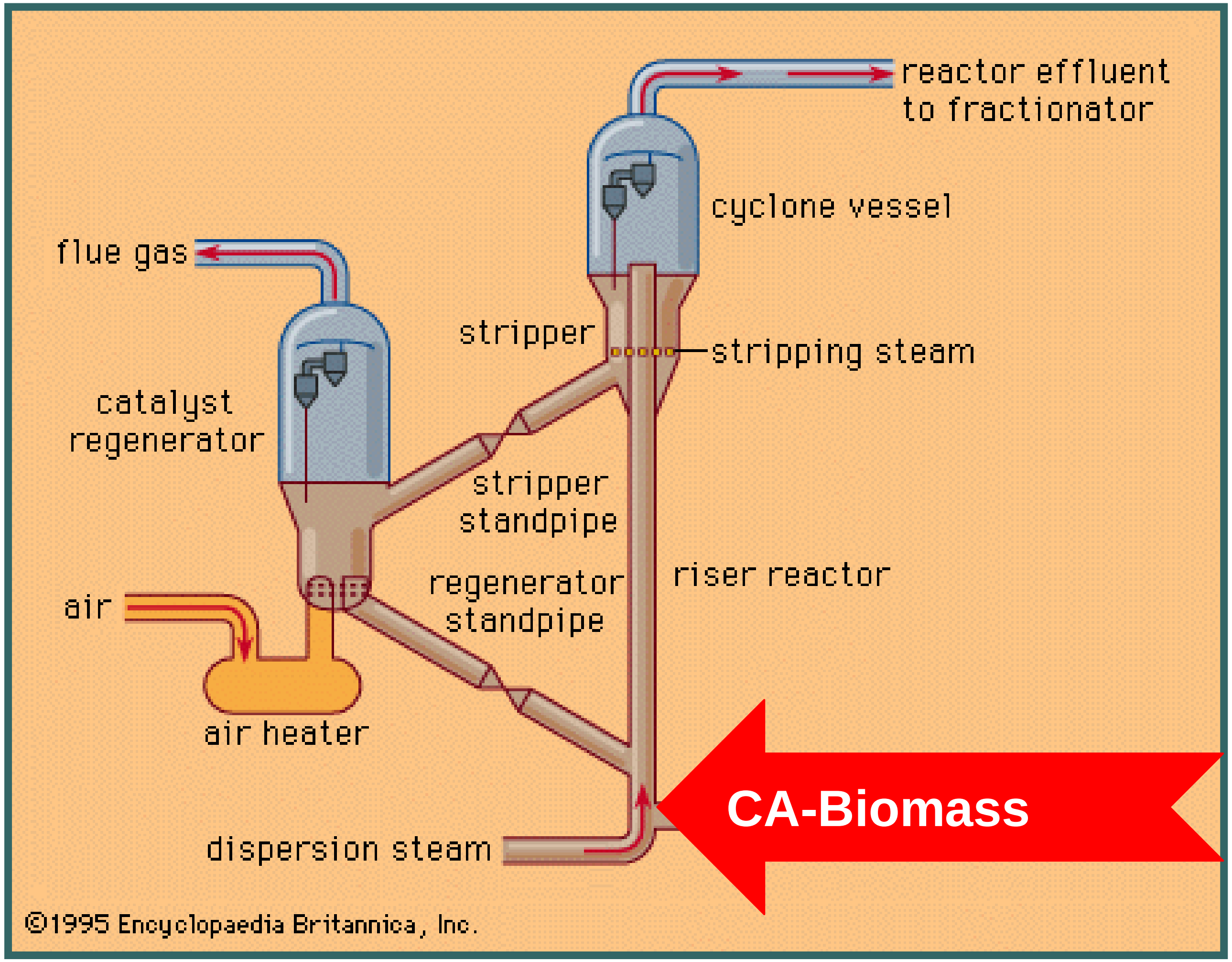
Pyrolysis to Sugars, Adsorption into catalyst



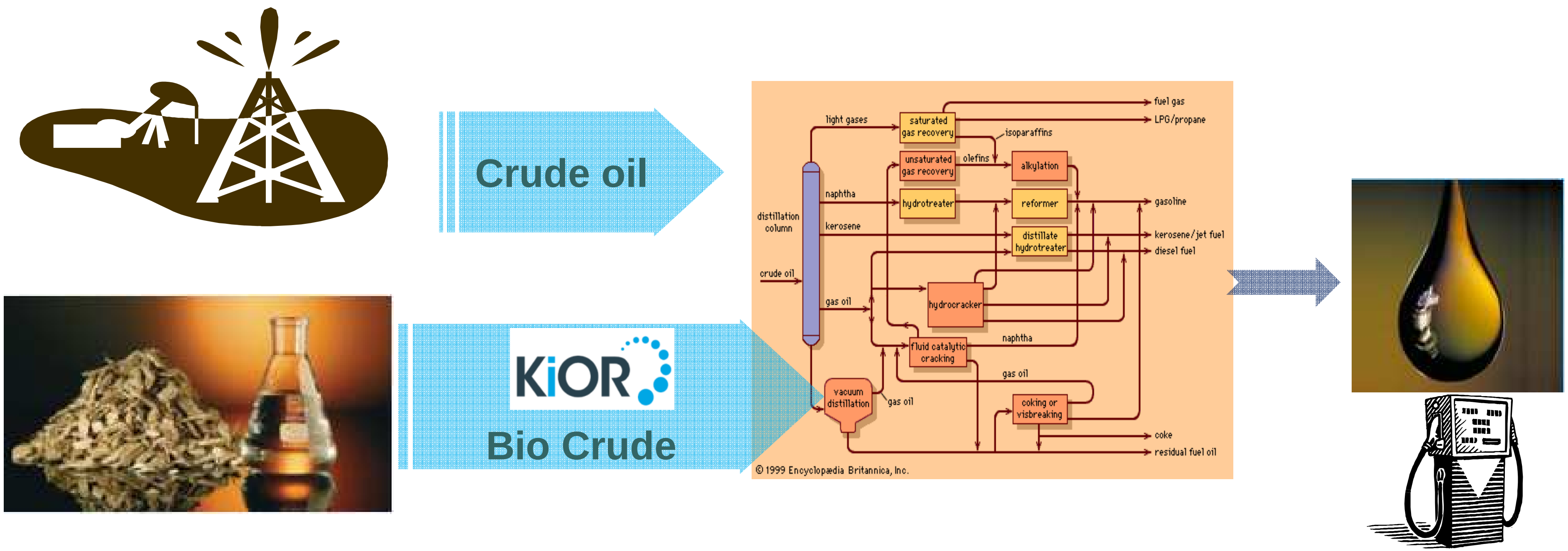
Catalytic Conversion

Gasoline, CO_2, Water

BCC = Biomass Catalytic Cracking



KiOR connects the Biomass and Oil Industry



- **Bio-Crude compatible with refining streams (but no Sulfur, metals etc)**
- **Technology based on existing refining technology**
- **Compatibility with existing infra-structure → lower entry barrier**

  → fast Time-To-Market!
- **KiOR creates feedstock diversity for oil refiners !**

Courtesy of Laurel Harmon, UOP

UOP Vision

Fuel Additives / Blends

Ethanol | Biodiesel

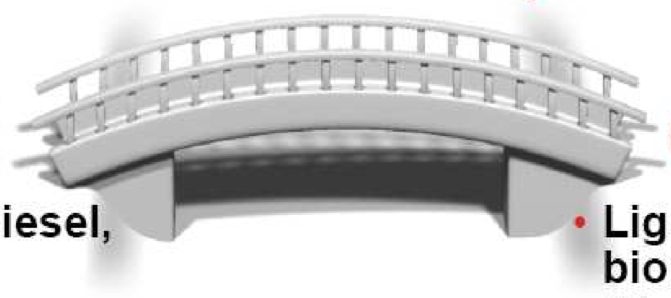
Fuels

Diesel | Gasoline

UOP's Bio-Fuels Technology Goals

Identify and utilize processing, composition, and infrastructure synergies to lower capital investment, minimize value chain disruptions, and reduce investment risk.

Inedible Oils: Jatropha



Generation 1

- **Vegetable oils to diesel, petrol and jet fuel**

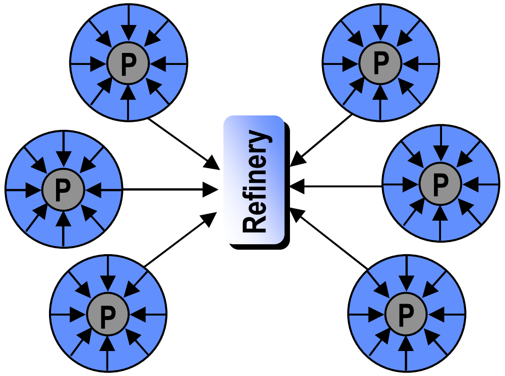
Generation 2

- **Lignocellulosic biomass to fuels**
- **Algal oils to fuels**

UOP 4941-10

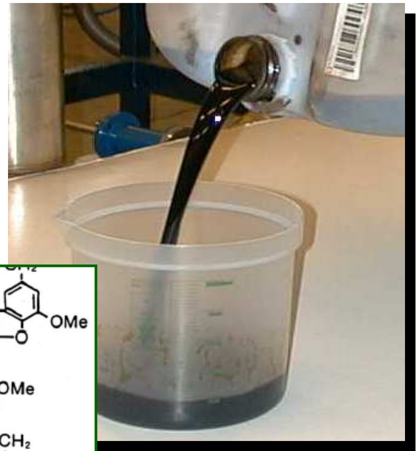
Lignocellulosic Biomass to Fuels Via Pyrolysis

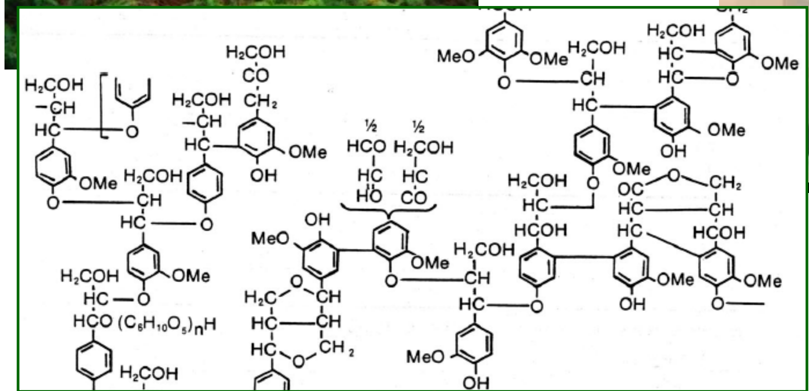
uop
A Honeywell Company



Biomass → Pyrolysis → Stabilization → Biocrude → Deoxygenate / Other Refinery Processes →

- Gasoline
- Diesel
- Jet
- Chemicals





Collaboration with DOE, NREL, PNNL
JV with Ensyn

Envergent’s Commercialization Plan

Biomass

‘Green’ Electricity

Fuel Oil

Available Now

Stage 1 Upgrader

Heating Oil
Marine Fuels

Stage 2 Upgrader

Transport Fuels

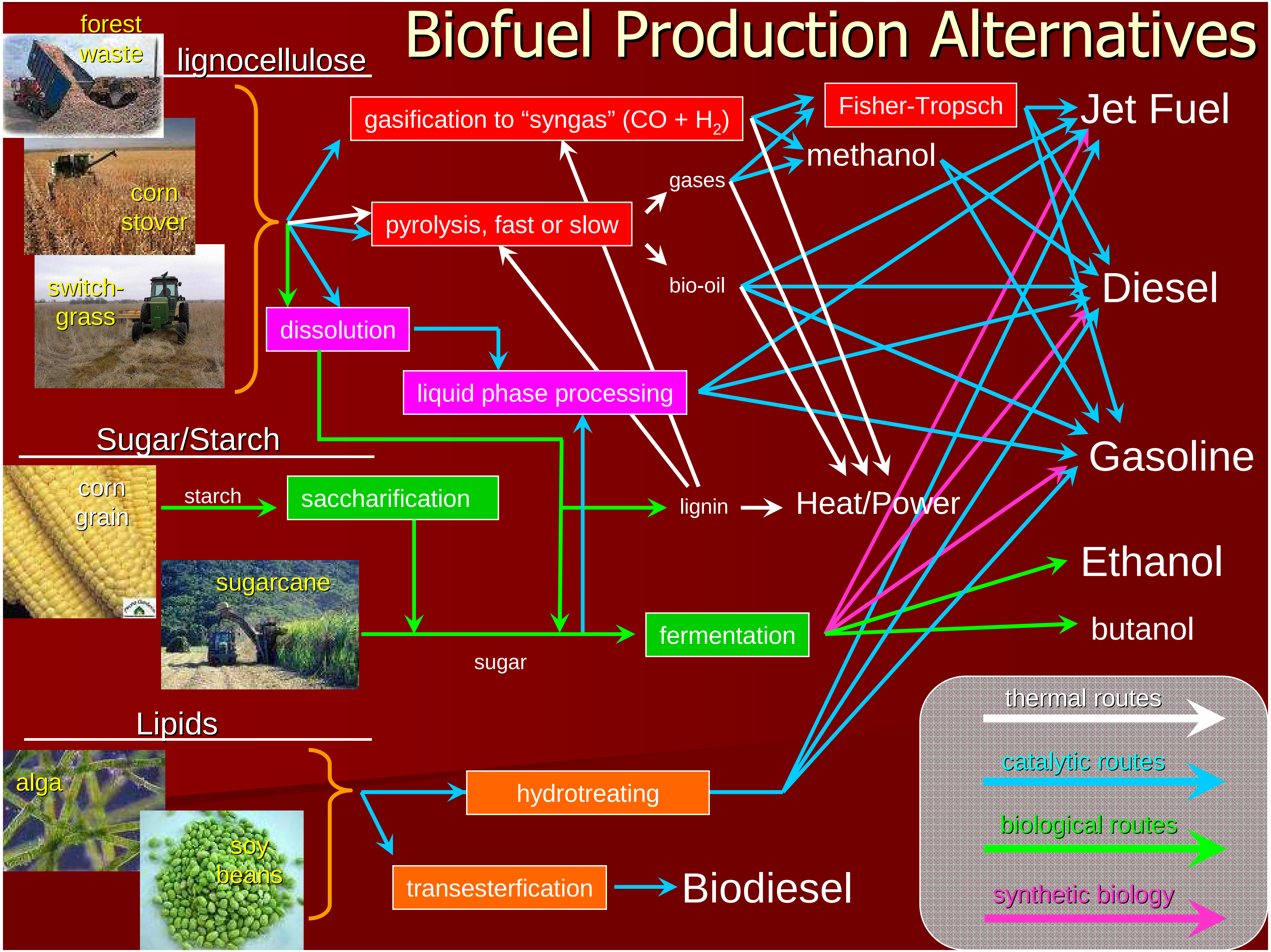
Timeline

2008

2009

2011

Rolling Deployment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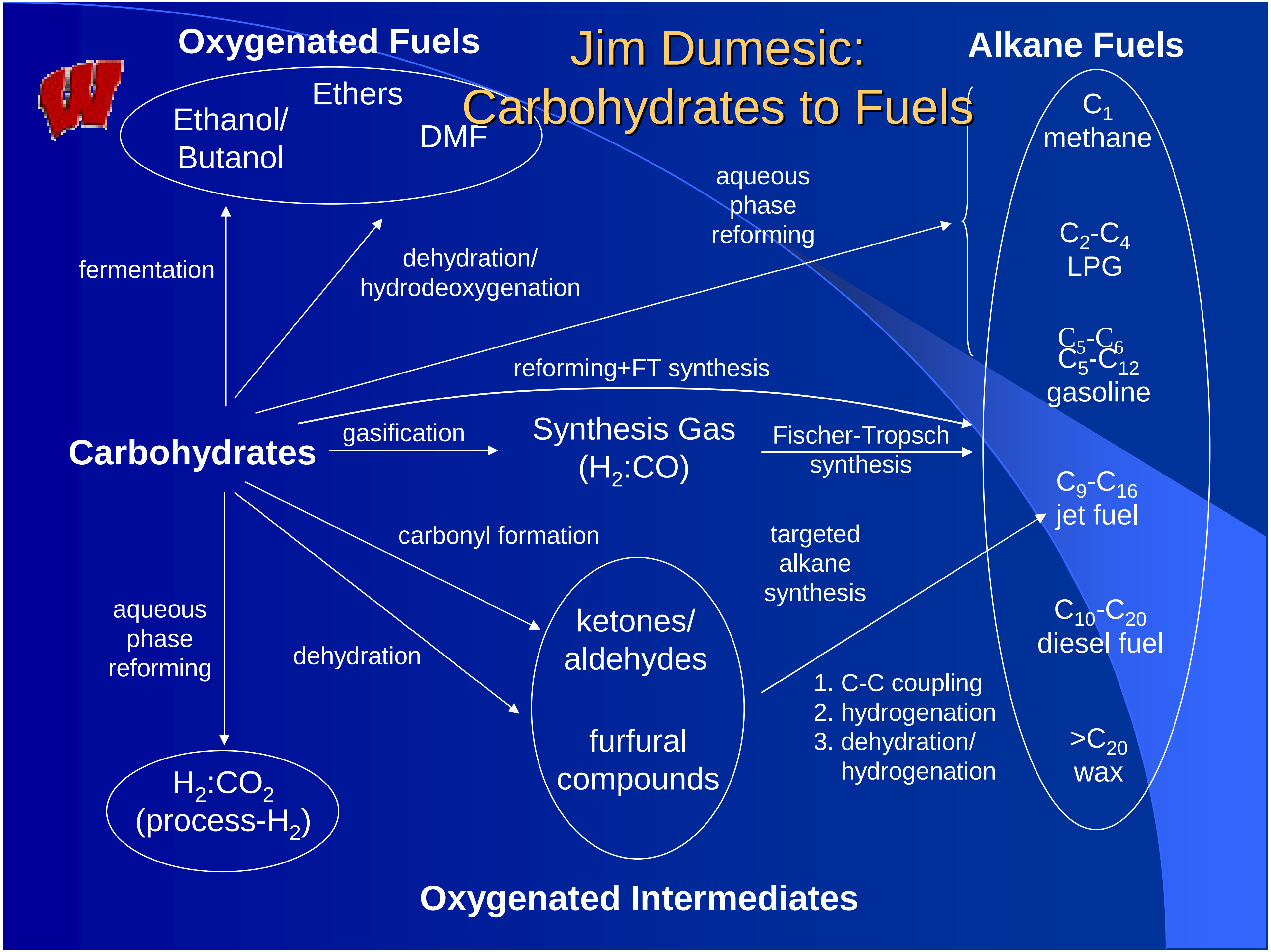


Jim Dumesic:
Carbohydrates to Fuels
Oxygenated Fuels
Ethanol/
Butanol
Ethers
DMF
Alkane Fuels
C_1
methane
C_2-C_4
LPG
C_5-C_6
C_5-C_{12}
gasoline
C_9-C_{16}
jet fuel
C_{10}-C_{20}
diesel fuel
>C_{20}
wax
fermentation
dehydration/
hydrodeoxygenation
aqueous
phase
reforming
reforming+FT synthesis
Carbohydrates
gasification
Synthesis Gas
(H_2:CO)
Fischer-Tropsch
synthesis
carbonyl formation
targeted
alkane
synthesis
aqueous
phase
reforming
dehydration
ketones/
aldehydes
furfural
compounds
1. C-C coupling
2. hydrogenation
3. dehydration/
hydrogenation
H_2:CO_2
(process-H_2)
Oxygenated Intermediates

Virent Energy Systems Overview

VIRENT

THE UNIVERSITY of WISCONSIN MADISON

WARF
Wisconsin Alumni Research Foundation

- Founded in 2002 by Dr. Randy Cortright and Professor Jim Dumesic from the Department of Chemical Engineering of the University of Wisconsin

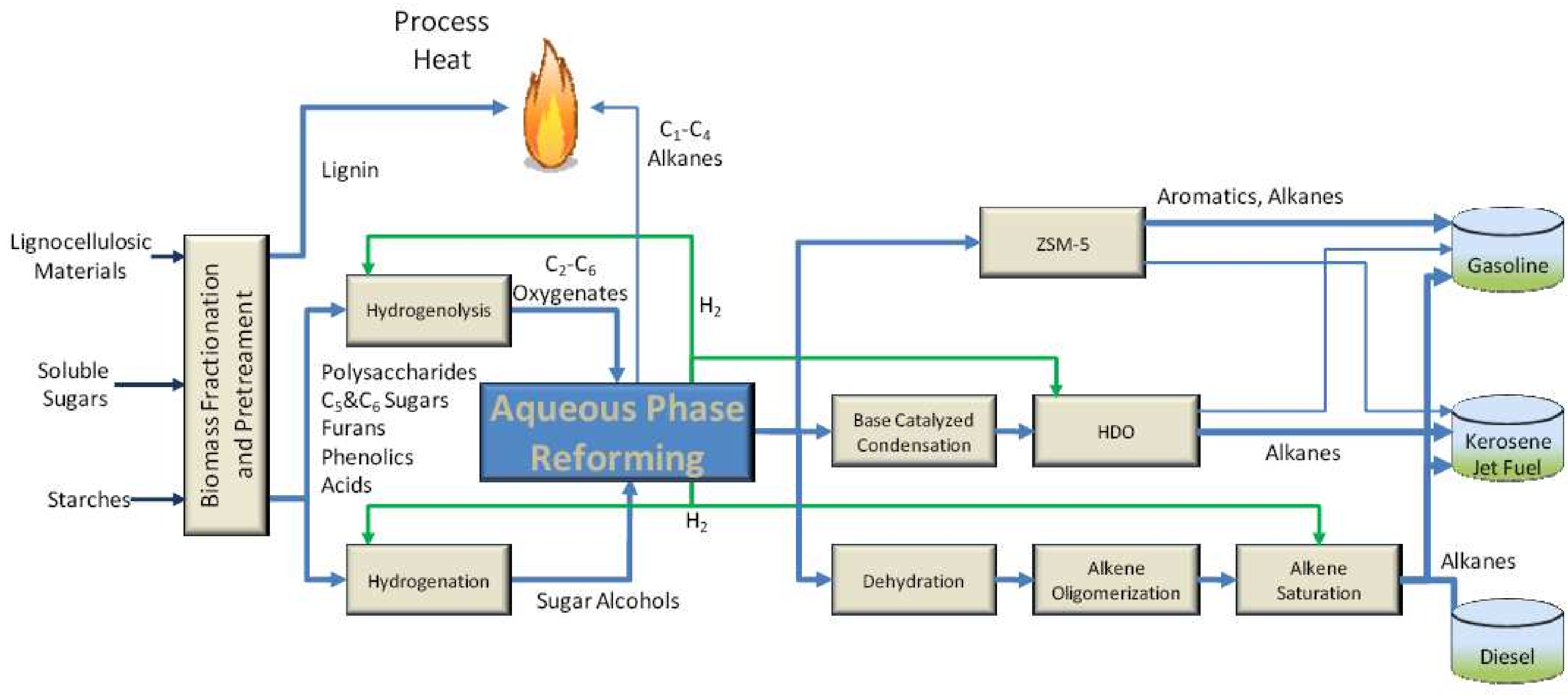
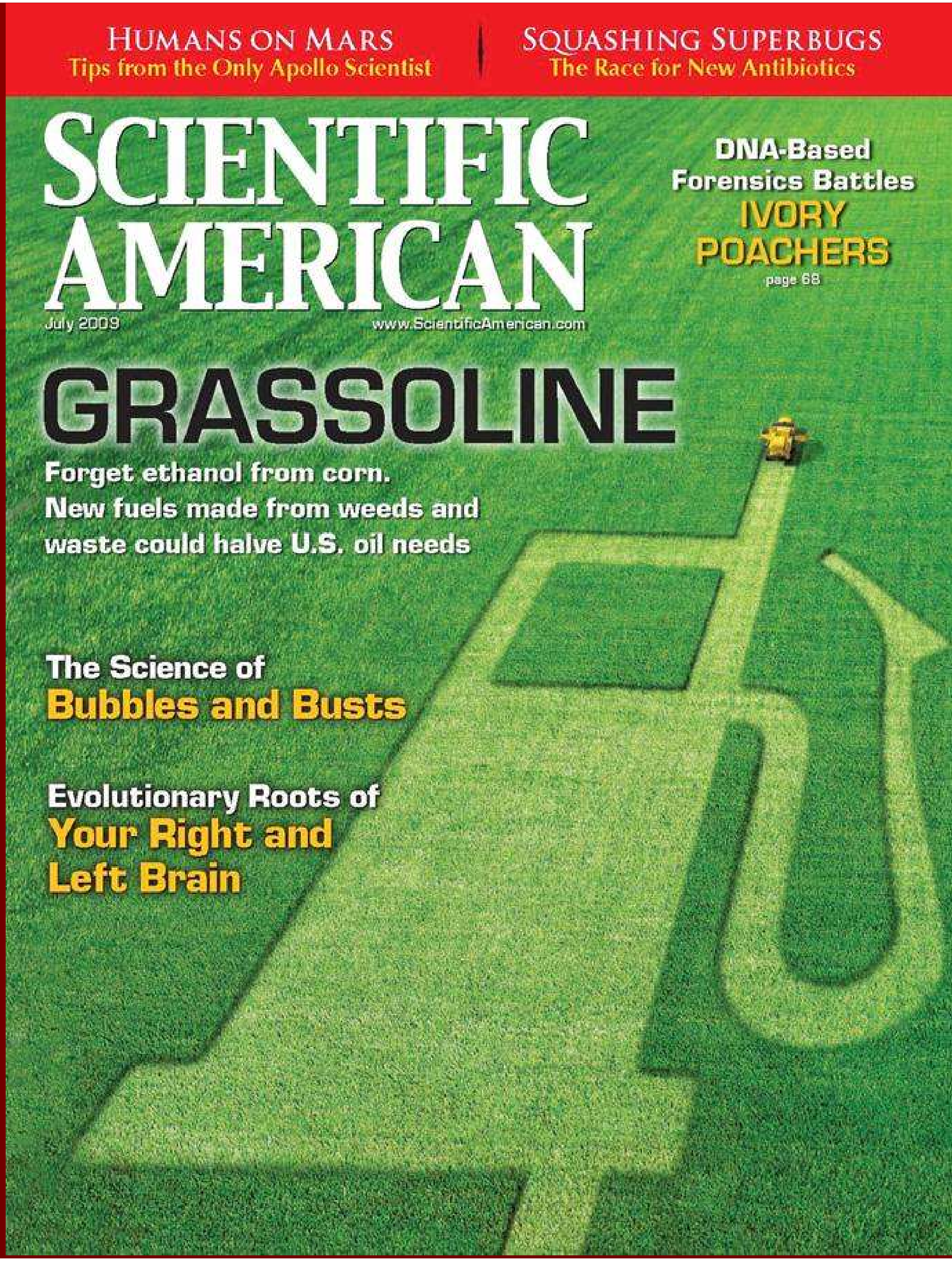


Figure 1. **Virent's BioForming® process to produce conventional liquid transportation fuels from biomass feedstocks. APR enables the process to partially defunctionalize carbohydrate feedstocks for further catalytic upgrading.**

Cane Sugar to Green Gasoline

VIRENT



HUMANS ON MARS
Tips from the Only Apollo Scientist
SQUASHING SUPERBUGS
The Race for New Antibiotics
SCIENTIFIC AMERICAN
July 2009
www.ScientificAmerican.com
DNA-Based Forensics Battles IVORY POACHERS
page 68
GRASSOLINE
Forget ethanol from corn.
New fuels made from weeds and waste could halve U.S. oil needs
The Science of Bubbles and Busts
Evolutionary Roots of Your Right and Left Brain

ENGINEERING

Cellulosic Biofuels: Got Gasoline?

Insert Deck Here

John R. Regalbuto

Most people think of ethanol as "the" liquid biofuel, and that the major advances in

nol to competitive levels.

Converting woody biomass to ethanol re-

plastics and pharmaceuticals. Virent Energy Systems developed a process known as Bio-

Virent – Shell: 100 MM GPY, 2014-2016

Envergent (UOP/Ensyn): 100 MM GPY, 2011 for license (major oils interested)

KiOR – (Petrobras): 100 MM GPY, 2011

Amyris - Crystalsev: ?? MM GPY, 2011

Choren: ?? MM GPY (FTS)

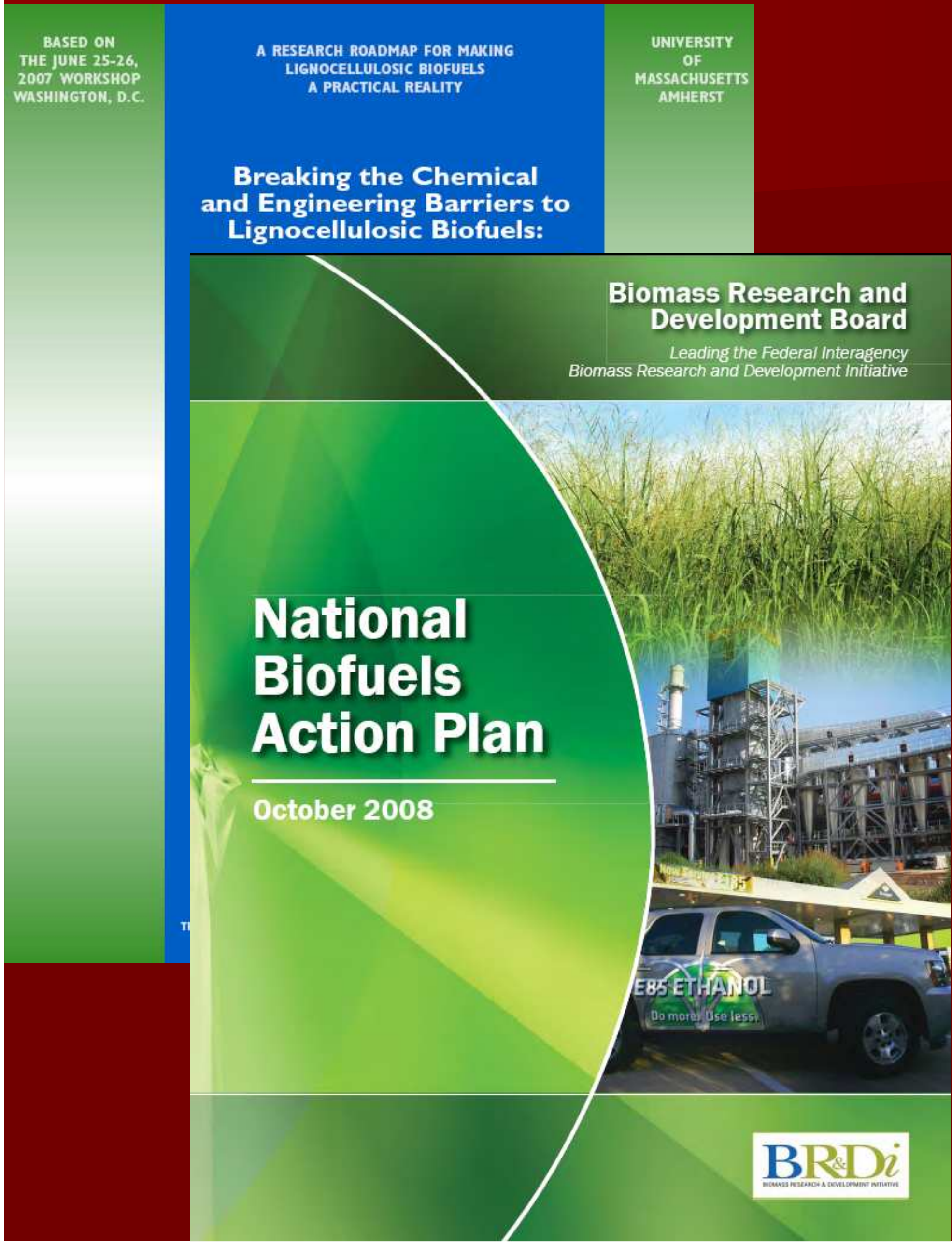
Saphire Oil (Algae): 100 MM GPY, 2016, 1 B GPY, 2022

woody biomass is a much more expensive

vances in the field of synthetic biology: mi-

mass to alcohols, these chemical methods

Current Status of Hydrocarbon Biofuels



- NBAP rewritten to include hydrocarbon biofuels
- Biomass Conversion Interagency WG → 10 Year RD&D Plan
- Sec. Chu has recently testified on priority of HC biofuels
- Federal Funding:
  - DOE/SC EFRCs; 2 or 3 on HCs
  - DOE/EERE/OBP: $800 MM, $480MM demonstration projects
  - NSF: "Hydrocarbons from Biomass" EFRI topic, $14-16 MM
  - USDA, DOD, etc.

Conclusions

- Green Gasoline vision: "Cellulosic Gasoline"
  - Utilize existing corn EtOH plants for blending at E10 (15 billion gal/yr)
  - With lignocellulose, make green gasoline, diesel, jet
    - Feedstocks exist, conversion costs coming down
  - Hydrocarbon biofuels from algae also possible
    - Feedstock production costs still too high; conversion is cheap
  - Recent indications: HYDROCARBON BIOFUELS ARE IMMINENT!

- Long range vision:
  - Light vehicles: electric or plug in hybrid (much less demand for gasoline)
  - Still need diesel and jet fuel for planes, trains, trucks, and boats
  - Use biomass for 100% of liquid transportation fuel

Summary Thoughts

- Green Gasoline vision: "Cellulosic Gasoline"
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  - Light vehicles: electric or plug in hybrid (much less demand for gasoline)
  - Still need diesel and jet fuel for planes, trains, trucks, and boats
  - Use biomass for 100% of liquid transportation fuels
- Process design, techno economic analysis, LCA are crucial

Current Situation in Biofuels

- U.S. oil consumption = 7 billion barrels of oil a year

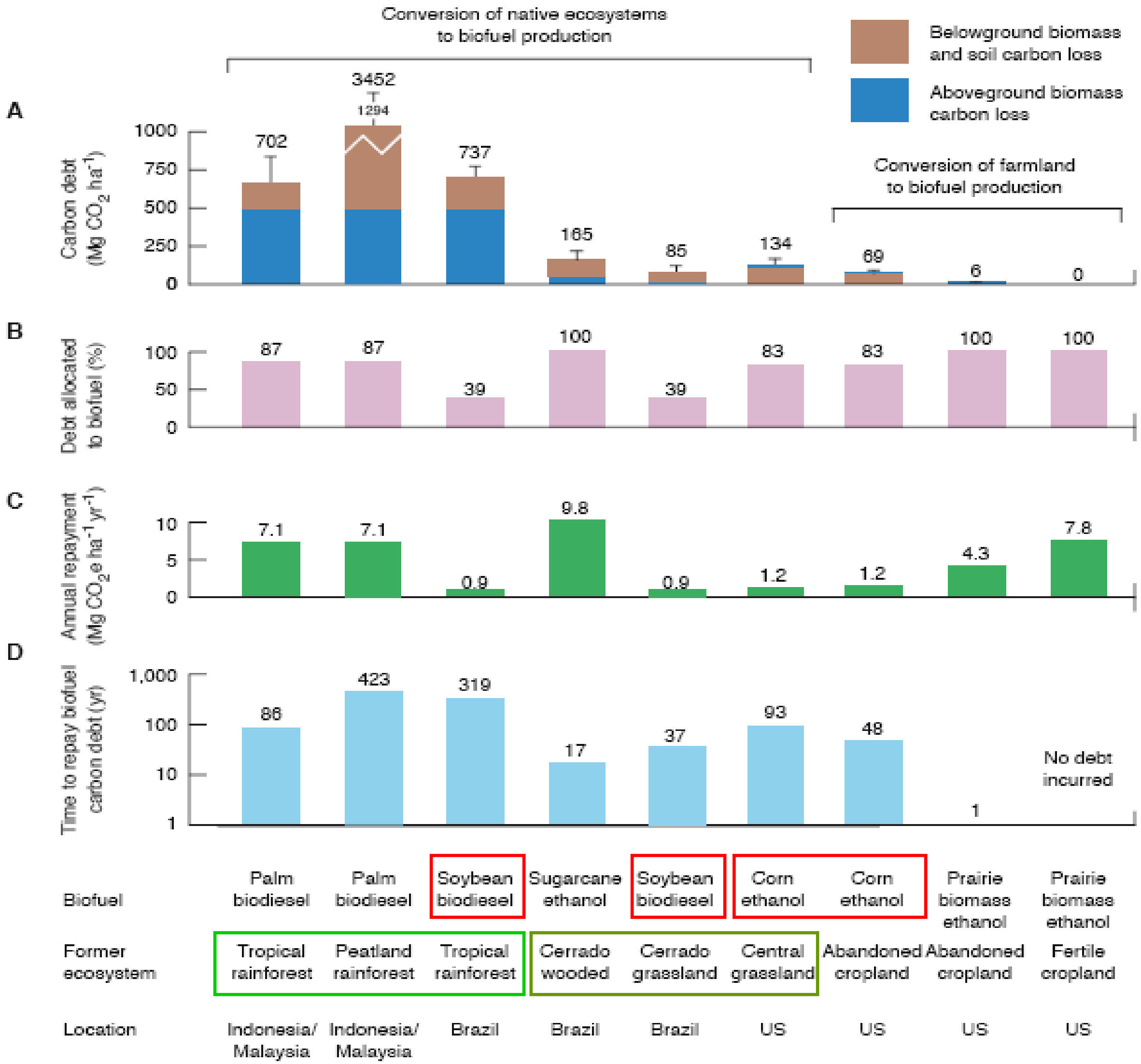
- DOE Billion Ton Study
  - 1.3 billion tons of biomass sustainably available
    - Forest waste
    - Agricultural residue
    - Energy crops (switch grass, short rotation poplar trees)

- Energy equivalent = 4 billion barrels of oil
  - Converted at 50% efficiency: 2 billion barrels = about half of imported oil

- Even when light-duty vehicles go electric or plug-in hybrid, need diesel and jet fuel for planes, trains, trucks, boats

Challenge 2:

Fargione et al; Land Use Change Penalty



- CO_2 debt is created when land is cleared
- This CO_2 debt can be considerable:
  - rainforest
  - woods or thick grassland
- Will take a long time to repay if:
  - land is heavily wooded
  - payback is slow (soy based diesel, corn ethanol)

Combined H_2 and Alkane Production

$C_6O_6H_{12} + 6\ H_2O \rightarrow 6\ CO_2 + 12\ H_2$ Aqueous Phase Reforming

$C_6O_6H_{12} + 7\ H_2 \rightarrow C_6H_{14} + 6\ H_2O$ Dehydration/Hydrogenation

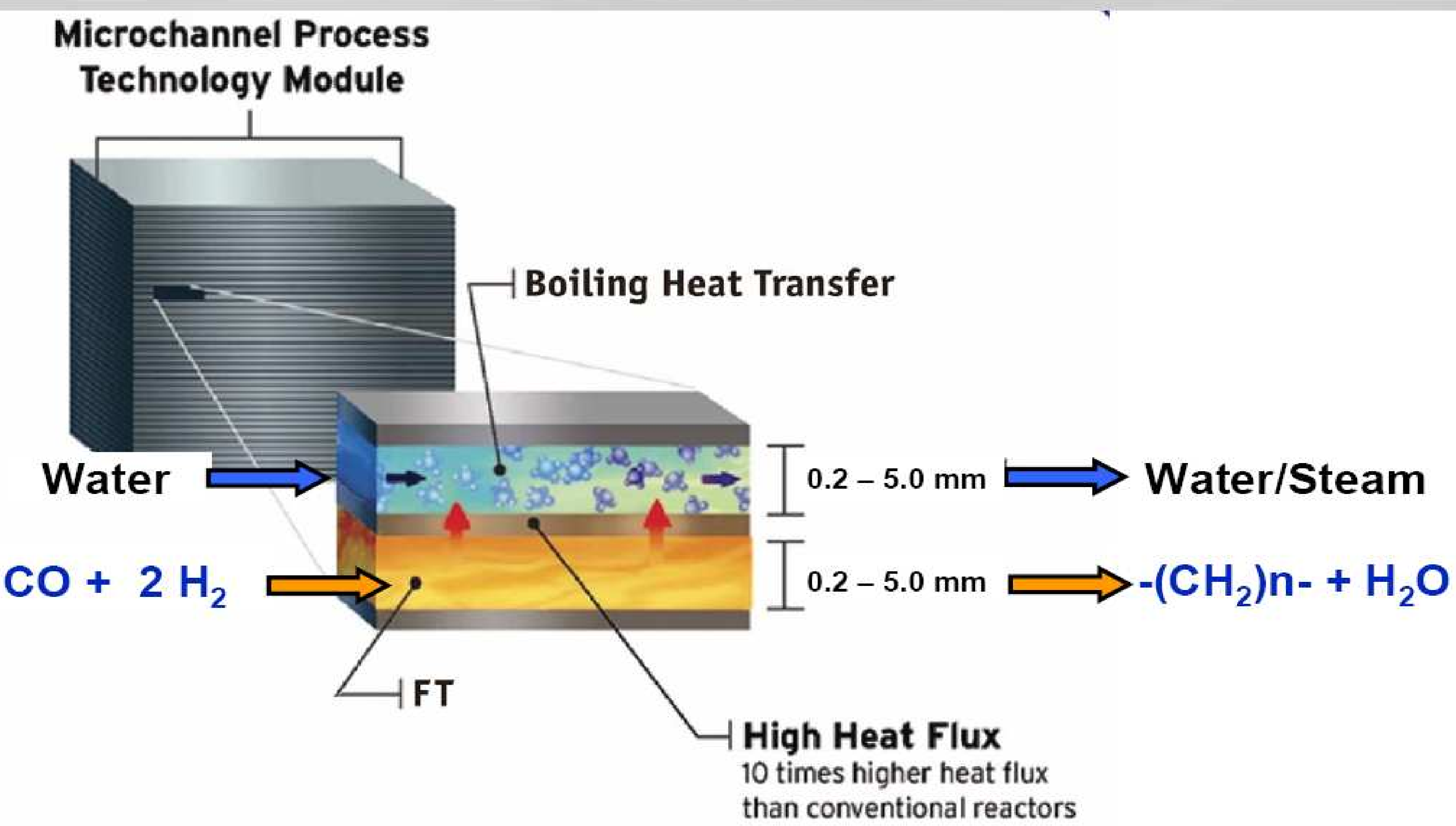
Combined reaction

$1.6\ C_6O_6H_{12} \rightarrow C_6H_{14} + 3.5\ CO_2 + 2.5\ H_2O$

Alkanes contain 95 % of the heating value and only 30 % of the mass of the biomass-derived reactant.

Huber, G.W.; Cortright, R.D.; and Dumesic, J.A.; "Renewable Alkanes by Aqueous-Phase Reforming of Biomass Derived Oxygenates", *Angewandte Chemie International Edition*, **43**, 1549-1551 (2004).

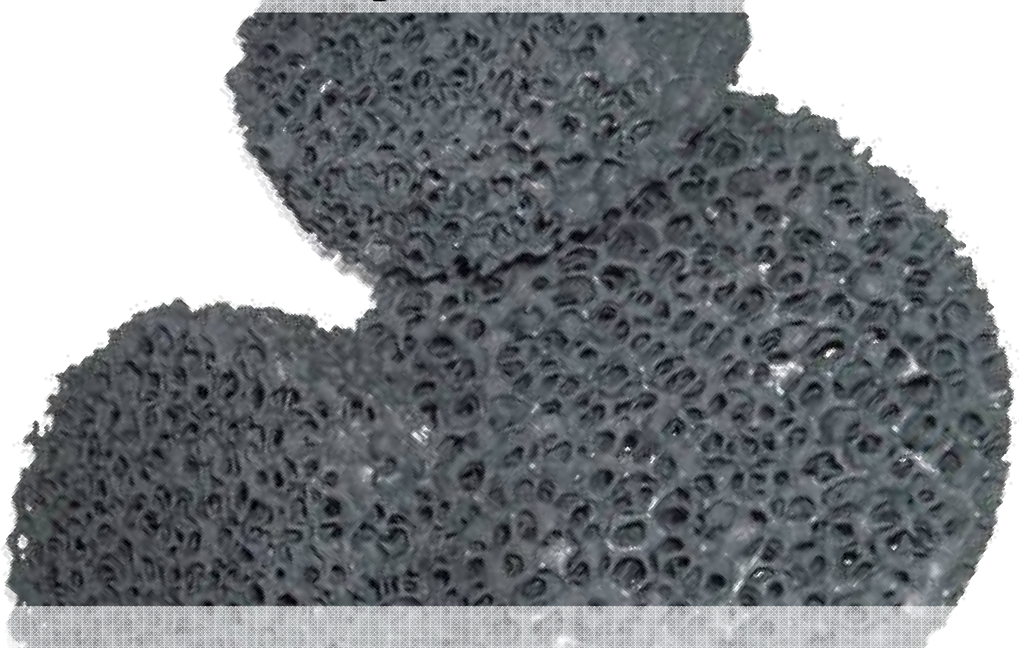
Microchannel Fischer-Tropsch Reactor Concept



Close integration of the exothermic Fischer-Tropsch synthesis and steam generation

DOE/SC/BES Funding

Catalytic Partial Oxidation of Biomass to Synthesis Gas



Joshua L. Colby, Paul J. Dauenhauer, Lanny D. Schmidt

University of Minnesota

Department of Chemical Engineering and Materials Science

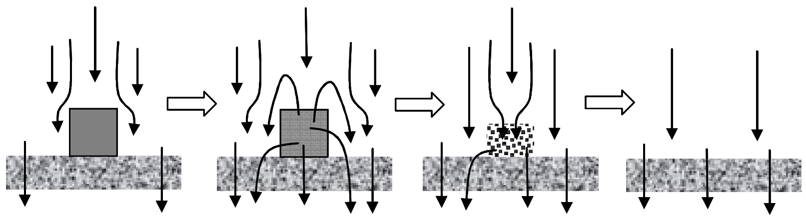
November, 20 2008

Process Overview

Chemistry

Volatilization: $(C_6H_{10}O_5)_n \rightarrow$ Gases + VOC + Char

Char + $O_2 \rightarrow$ Gases



Oxidation: VOC + $O_2 \rightarrow$ Gases

Reforming: VOC + $H_2O \rightarrow$ Gases

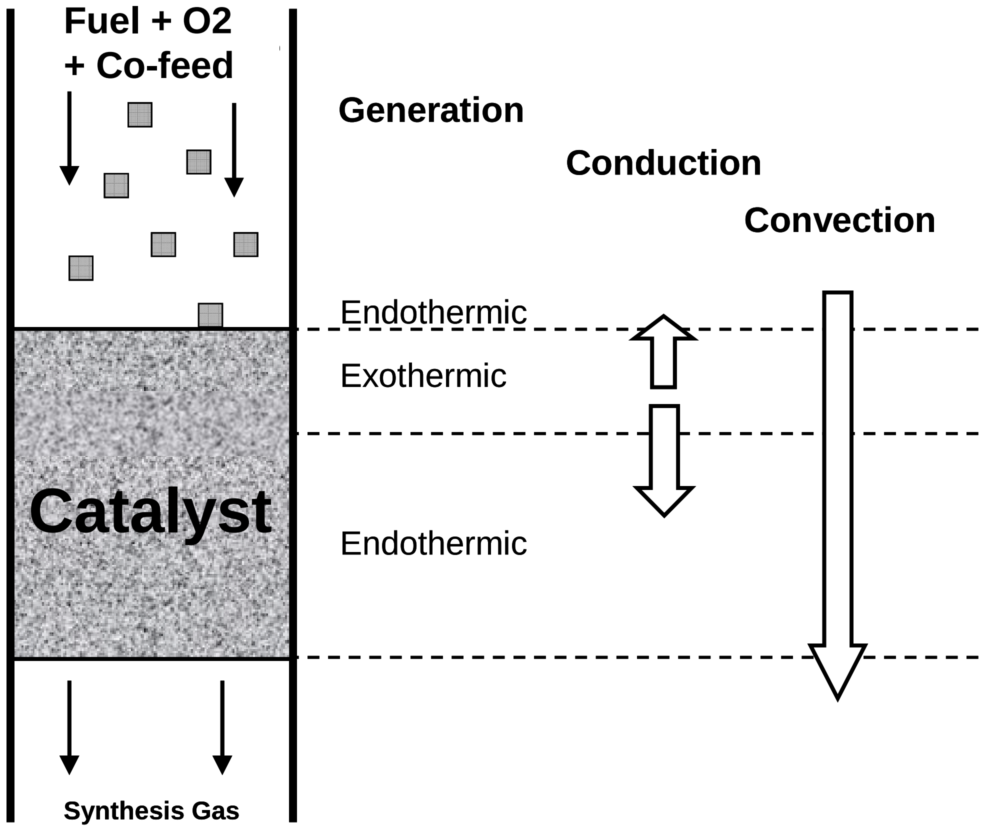
$CO + H_2O \leftrightarrow CO_2 + H_2$

Global Chemistry:

$(C_6H_{10}O_5)_n + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + H_2O$

Reactor

Heat



CPOx of Cellulose w/ Steam

Biomass

↓

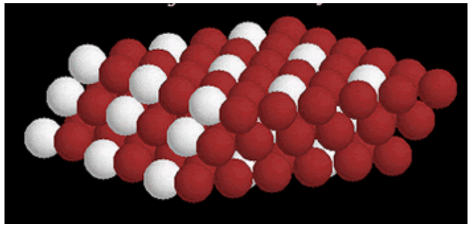
Drying/Grinding/Pretreatment

↓

One-Step Catalytic Gasification

↓

Power | Synthesis → Fuel Separation

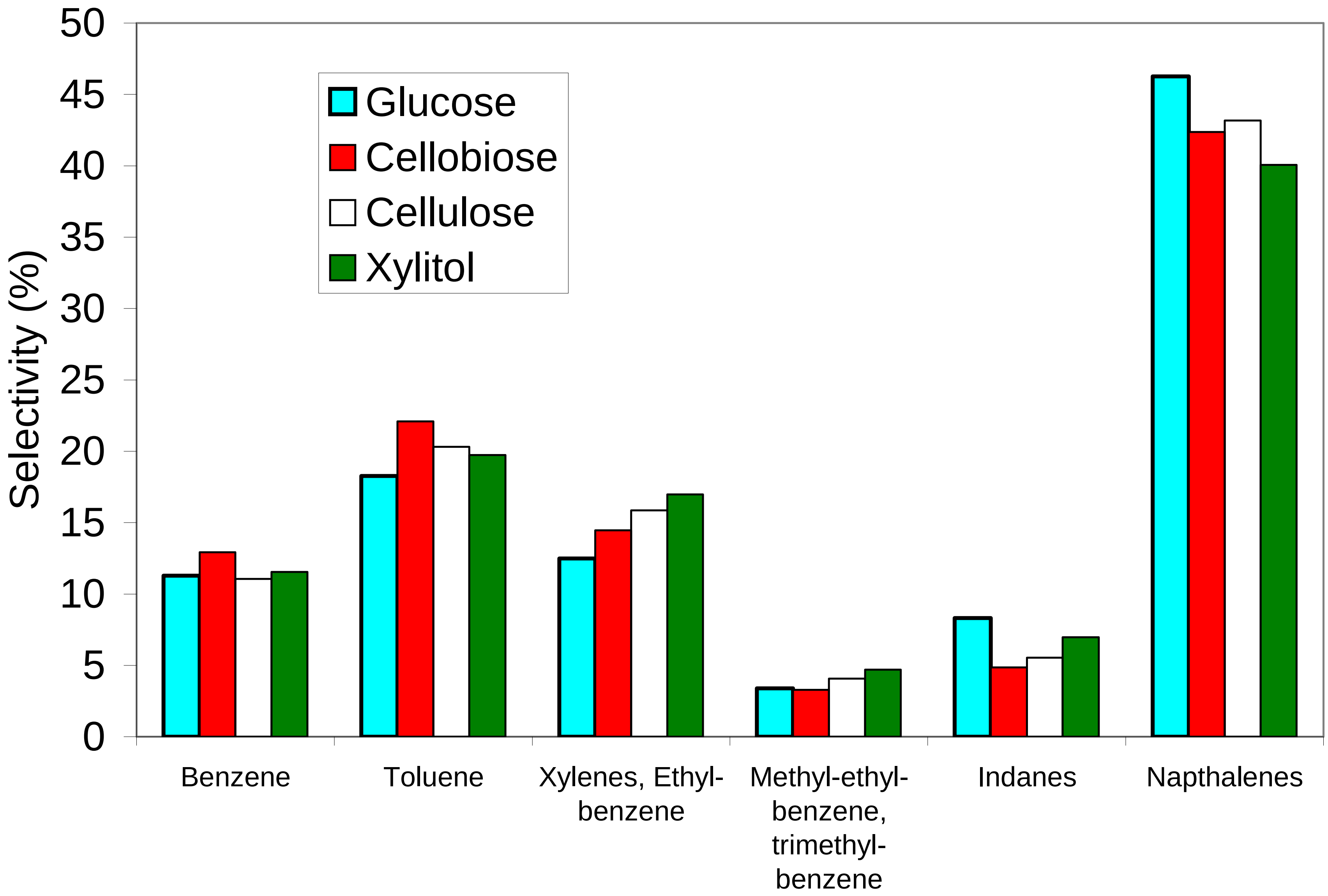


www.engr.wisc.edu/che/

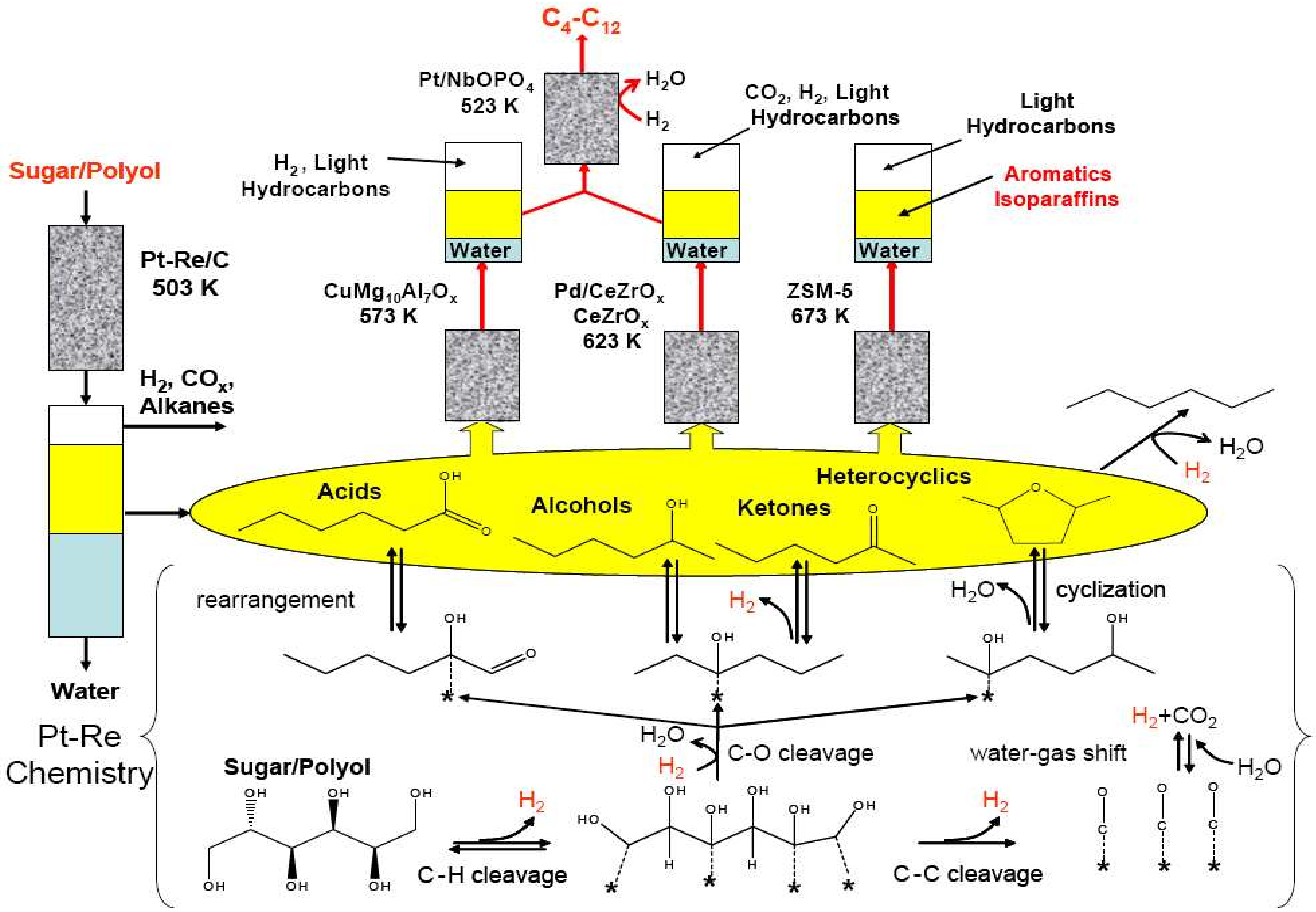
www.bp.com

UMassAmherst

Aromatic Selectivity

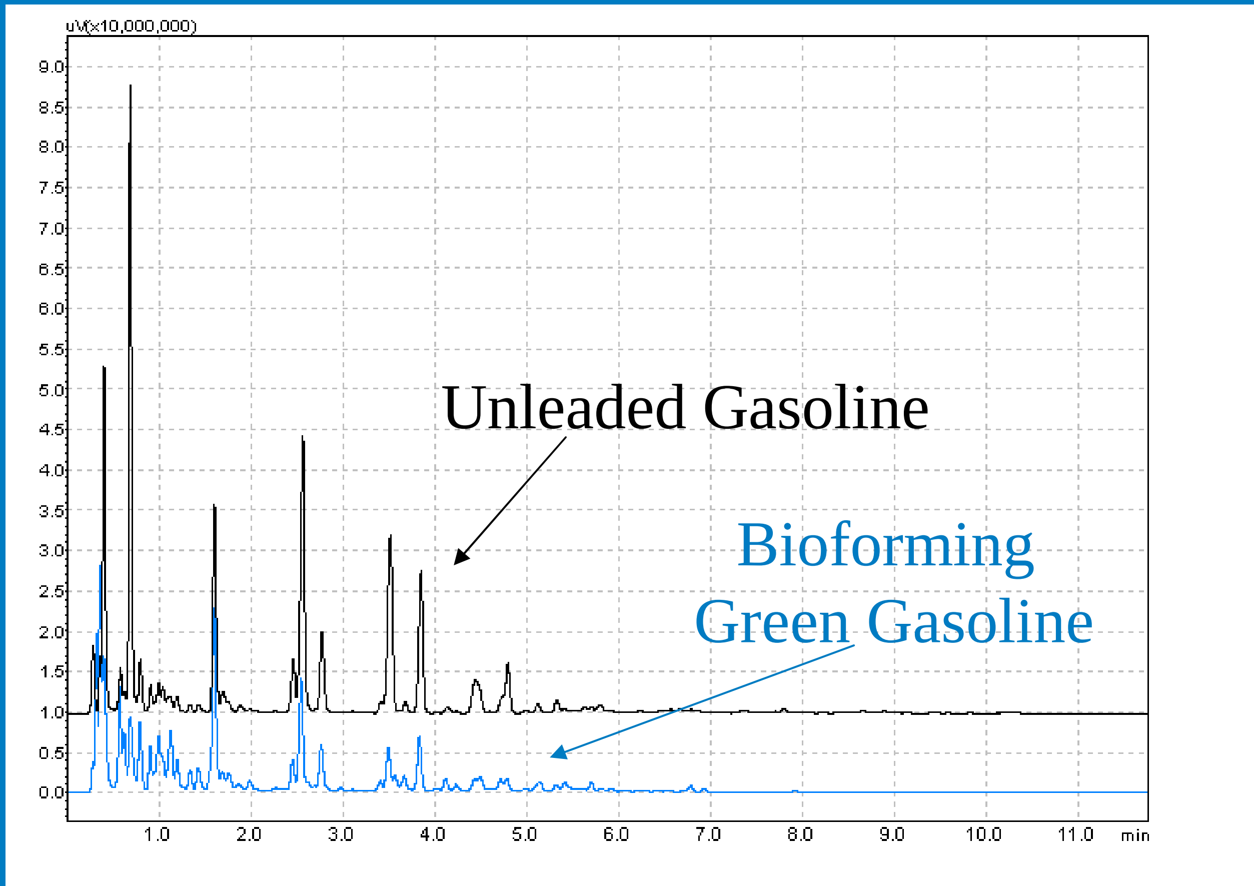


Jim Dumesic: Science October Issue



Green Gasoline Composition

Same Components as Standard Unleaded Gasoline

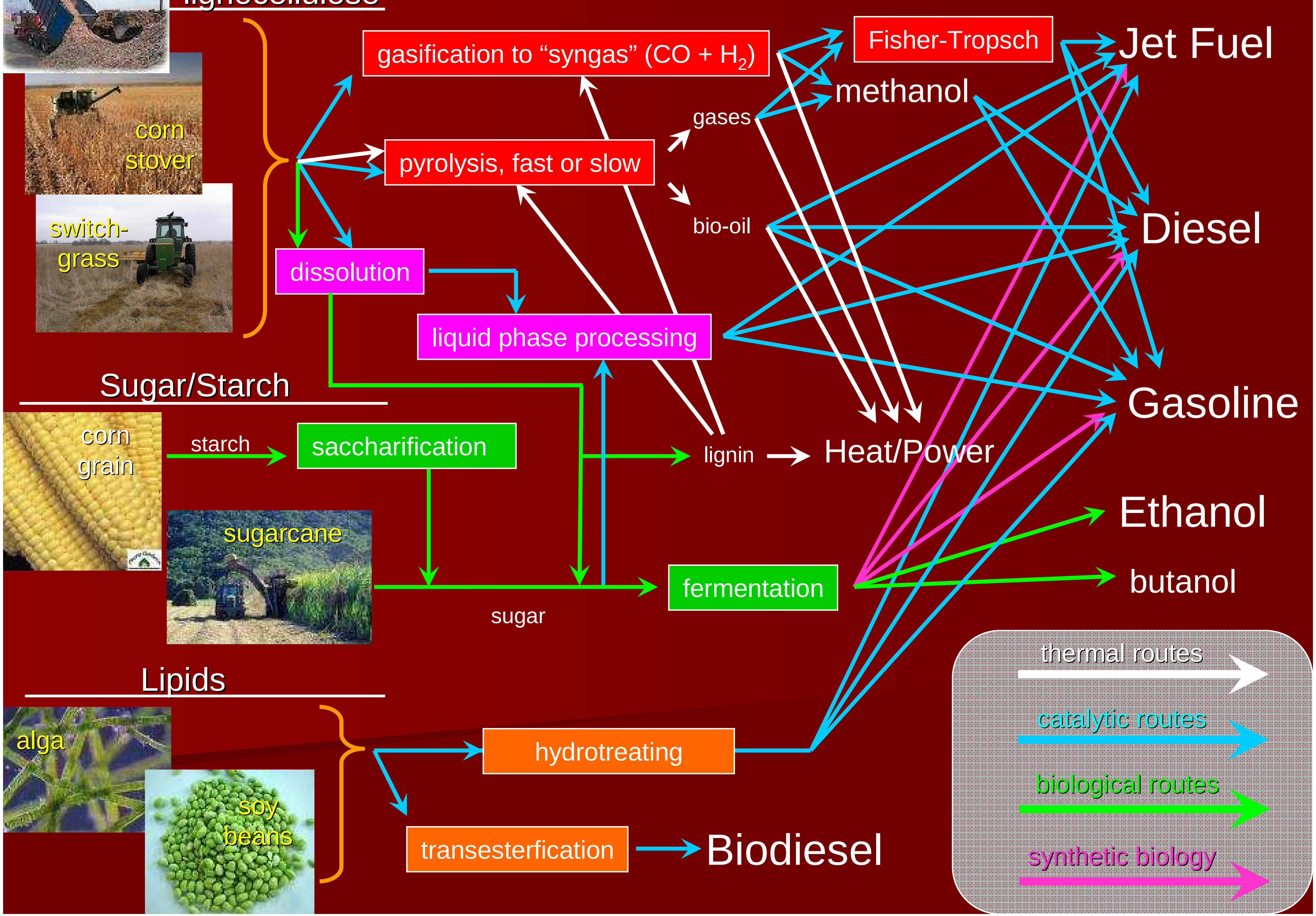


Unleaded Gasoline
115,000 BTUs/Gal

Bioforming
Green Gasoline
115,000 BTUs/Gal

Ethanol
76,000 BTUs/Gal

Biofuel Production Alternatives



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THE BEST REPLACEMENT FOR PETROLEUM IS PETROLEUM

RENEWABLE.

OUR FOUNDERS ASKED:

"If you removed all constraints, what would the ideal biofuel be?"

THEIR ANSWER: petroleum.

A biological, fermentation-based process starting from renewable sugars offers the most compelling economics. However, petroleum products could not be made in this way. Until now.

LS9 Renewable Petroleum™ technology enables the rapid and widespread adoption of renewable transportation fuels. Patent-pending DesignerBiofuels™ products are custom engineered to have higher energetic content than ethanol or butanol; to have fuel properties that are essentially indistinguishable from those of gasoline, diesel, and jet fuel; and to be distributed in existing pipeline infrastructure and run in any vehicle. Learn more about LS9

What is Renewable Petroleum™ Technology?

Learn about our DesignerBiofuels™ Products

Join Our Team!

Renewable Petroleum™ Technology

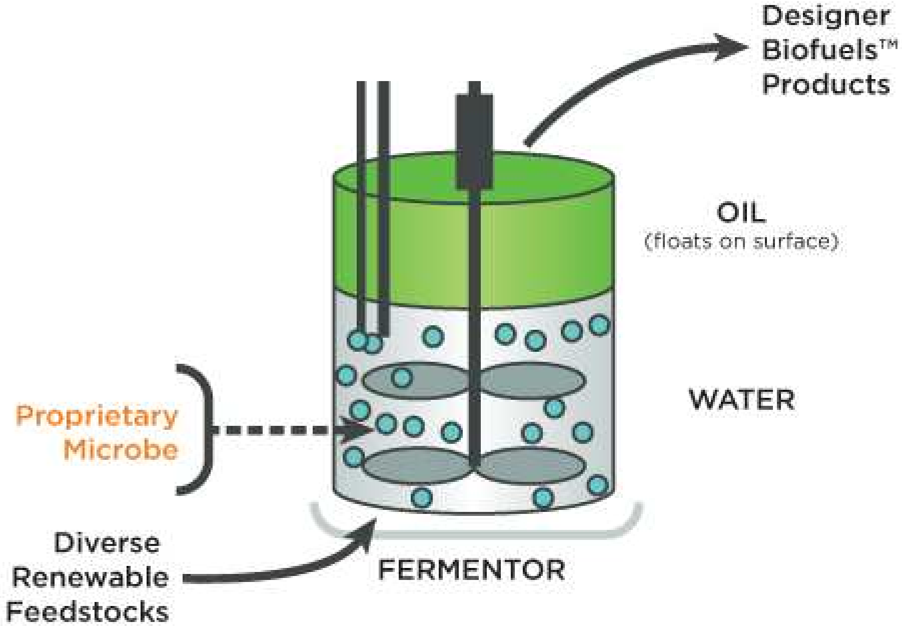
LS9's patent-pending technologies will transform the transportation fuel market. These breakthroughs will offer a commercially attractive path to sustainability.

— Noubar Afeyan
Managing Partner and CEO
Flagship Ventures

Petroleum, on which modern day society was built and is now dependent, is a diminishing resource with increasing environmental, political, and economic disadvantages.

The ideal alternative would be chemically identical to petroleum, allowing broad and rapid adoption, derived from renewable resources, scalable to support current and future demands, domestically derived, and cost competitive without subsidies.

LS9 has developed Renewable Petroleum™ technologies to meet this need.



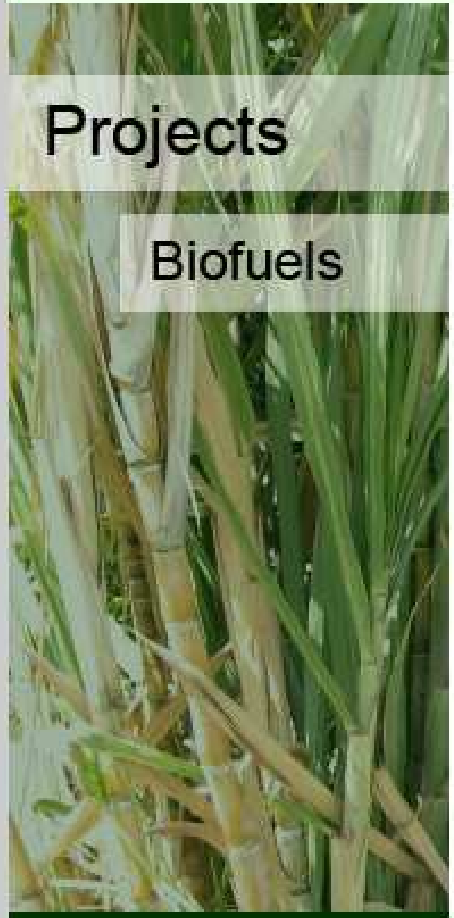
Pushing the frontiers of synthetic biology and industrial biotechnology, LS9 has created industrial microbes that efficiently convert renewable feedstocks to a portfolio of "drop in compatible" hydrocarbon-based fuels and chemicals. LS9's unique technology provides a means to genetically control the structure and function of its fuels, enabling a product portfolio that meets the diverse demands of the petroleum economy.

LS9 has developed a new means of efficiently converting fatty acid intermediates into petroleum replacement products via fermentation of renewable sugars. LS9 has also discovered and engineered a new class of enzymes and their associated genes to efficiently convert fatty acids into hydrocarbons. LS9 believes this pathway is the most cost, resource, and energy-efficient way to produce hydrocarbon biofuels and petroleum-replacement products. This translates into efficient land and feedstock use and directly addresses tensions between food versus fuel production.

AMYRIS BIOTECHNOLOGIES

Realizing the Promise of Synthetic Biology

COMPANY PROFILE TECHNOLOGY CURRENT PROJECTS NEWS CAREERS



New Technology for Energy Needs: Cost-Effective, Renewable Biofuels

Amyris Biotechnologies is developing a large-scale fermentation process to renewably produce biofuels. Amyris is developing a gasoline substitute that contains more energy than ethanol, will result in lower cost and less polluting biofuel blends, and is fully compatible with today's cars and the existing petroleum infrastructure. We are also developing a diesel substitute that can achieve lower costs and much greater scale than vegetable oil based biodiesels. Our next generation biodiesel is inherently stable in cold temperatures and does not break down during storage and transport like conventional biodiesel. Both our gasoline substitute and our diesel substitute will be made from the same feedstocks and production plants that are used to make ethanol.

Amyris is supported in this work by funding from Khosla Ventures, Kleiner Perkins Caufield & Byers, and TPG Biotech.

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News

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April 23, 2008

Amyris and Crystalsev Join to Launch Innovative Renewable Diesel from Sugarcane by 2010

New Fuel Works in Today's Engines, Reduces Emissions by 80 Percent

SAO PAULO, Brazil, and Emeryville, California, USA - Amyris, the leading innovator of next-generation renewable fuels, and Crystalsev, one of Brazil's largest ethanol distributors and marketers, today announced plans to commercialize advanced renewable fuels made from sugarcane including a diesel, jet fuel and gasoline. The first product, a renewable diesel that works in today's engines, is targeted for commercialization in 2010. Scale-up and testing work to date indicate that this fuel scales more quickly and economically than currently available biofuels, and reduces emissions by 80 percent over petroleum diesel.

Using Amyris' breakthrough technology platform, the new joint venture, Amyris-Crystalsev Pesquisa e Desenvolvimento de Biocombustiveis Ltda, will work with Brazilian sugarcane mills and fuel producers to quickly scale production of the Amyris renewable diesel fuel. Amyris will hold the majority stake in the Amyris-Crystalsev venture, and Crystalsev will hold the remaining stake and contribute commercialization expertise.

Santelisa Vale, the second largest ethanol and sugar producer in Brazil and majority owner of Crystalsev, has contracted to provide two million tons of sugarcane crushing capacity and plans to adopt the new technology beginning at its flagship mill - Santelisa. Santelisa Vale will also provide technical and engineering expertise to accelerate development and scale-up of the Amyris fuel. The Amyris-Crystalsev venture plans to bring other sugar producers into the fold as it launches its diesel fuel and progresses on new products.

"This partnership represents a historic first for the global transportation fuels industry. By securing a significant supply of the most sustainable feedstock and collaborating with our world renowned partners Crystalsev and Santelisa, we now have the ability to take our pioneering technology out of the lab and rapidly scale production toward supplying the needs of the worldwide renewable fuels market," said John Melo, CEO Amyris.

Unlike current biofuels, Amyris renewable fuels are designed to meet or exceed the quality of existing petroleum fuels and be fully compatible with existing fuels infrastructure and engines. They are formulated biologically through sugar fermentation to create hydrocarbons, the same molecular structure found in traditional petroleum fuels. The result is a new kind of renewable fuel that is expected to work in today's automotive and jet engines with no performance trade-offs, to blend at high-levels with other petroleum fuels, and to be fully compatible with existing distribution infrastructure, while offering advantages of significantly reduced emissions.

Potential advantages of hydrocarbons

- Self-separation from water - no distillation required. Less energy input:
  - lowers processing cost
  - improves the C balance
- ~30% higher energy density; won't suffer a commensurate loss of gas mileage
- Reduction of water use
- Green gasoline/diesel/jet fuel fit into current infrastructure; no need for engine modifications or new distribution systems