An NSF Perspective on

Next Generation Hydrocarbon Biofuels:

Implications on Land and Water Use

Atibaia, Brazil

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August 10th, 2009
Challenge 1: Avoid Land Use Change Penalty

- Land use change creates a large CO\textsubscript{2} debt
- Payback can be very slow
Challenge 1: Fargione et al; Land Use Change Penalty

- CO₂ debt is created when land is cleared
- This CO₂ 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)
Avoidance of Land Use Change Penalty

- Use fallow/abandoned farmland and marginal land with high debt-paying energy crops:
  - Lignocellulose:
    - Switchgrass
    - Poplar trees

- Avoid land use change altogether:
  - Forest waste
  - Agricultural residue

**Optimal regime of operation**

- Time "banked"
- Energy crops on marginal land
- Forest waste and ag residue

**Conversion of native ecosystems to biofuel production**

**Conversion of farmland to biofuel production**

**Graphs and data**

- **A**: Carbon debt (Mg CO₂ ha⁻¹)
  - Use fallow/abandoned farmland and marginal land with high debt-paying energy crops:
  - Lignocellulose:
    - Switchgrass
    - Poplar trees

- **B**: Debt allocated to biofuel (%)
  - Avoid land use change altogether:
    - Forest waste
    - Agricultural residue

- **C**: Annual repayment (Mg CO₂ e ha⁻¹ yr⁻¹)
  - Forest waste and ag residue

- **D**: Time to repay biofuel carbon debt (yr)
  - Optimal regime of operation
Current U.S. 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
Current U.S. 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 → 18 MPG
    - Renewable fuels must be exempted from CAFE increase

Challenge 2:
Produce a renewable biofuel without incurring a loss in gas mileage.
The Solution:

- Produce hydrocarbon biofuels from lignocellulose grown with minimal land use change
  - incur penalties in neither gas mileage nor lifecycle greenhouse gas emissions
  - utilize existing fuel infrastructure (pipelines, refineries, storage tanks, engines)

- “Cellulosic Gasoline” or green gasoline
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
More fuel from sugar cane without additional land or water use:

- Produce ethanol from cane juice
- What if we could produce diesel from bagasse?
Roadmap for Hydrocarbon Production

- 2007 NSF/ENG and DOE/EERE Cosponsored Workshop in June, 2007

- Final Report Released April 1, 2008
  - [www.ecs.umass.edu/biofuels/roadmap.htm](http://www.ecs.umass.edu/biofuels/roadmap.htm)

- Input for Interagency Working Group on Biomass Conversion, National Biofuels Action Plan
The Catalyst: Heart of a Catalytic Converter

Pt/Rh/Al$_2$O$_3$ catalyst

washcoat

NO + CO $\rightarrow$ N$_2$ + CO$_2$
Catalysts: Heart of Petroleum Refineries
Fuels, Chemicals, Materials (Textiles)
Biofuel Production Alternatives

- Gasification to “syngas” (CO + H₂)
- Pyrolysis, fast or slow
- Liquid phase processing
- Dissolution
- Saccharification
- Fermentation
- Hydrotreating
- Transesterification
- Biodiesel

Jet Fuel
- Methanol
- Gasoline
- Ethanol
- Diesel
- Butanol

Lipids
- Algae
- Soybeans

Sugar/Starch
- Corn grain
- Starch
- Sugarcane
- Sugar

Forest waste
- Switchgrass
- Corn stover

Lignocellulose

Thermal routes
- Catalytic routes
- Biological routes
- Synthetic biology

Heat/Power

Fisher-Tropsch
BioMax – Independent Energy Solution
On-site Electricity, Heat, and Synthetic Liquid Fuels from Biomass

Power Generation Module (Genset)

Gas Production Module

Biomass

Combustible Gas (Boiler/Dryer/Furnace/Chiller)

Liquid Fuels

Gas-To-Liquid Module

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

25 Gallons of Syndiesel / Day Per 0.5 Tons of Biomass
Microchannel Fischer-Tropsch Reactor Concept

Note: water positive reaction

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

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- Forest waste
- Corn stover
- Switchgrass
- Corn grain
- Sugarcane
- Alga
- Soy beans

- Jet Fuel
- Diesel
- Gasoline
- Ethanol
- Butanol

- Fisher-Tropsch
- Methanol
- Bio-oil
- Lignin

- Thermal routes
- Catalytic routes
- Biological routes
- Synthetic biology

- Sugar/Starch
- Lipids
- Saccharification
- Dissolution
- Heat/Power

- Butanol
- Biodiesel
Gasoline from Cellulose by Catalytic Fast Pyrolysis in a Single Reactor

Note: water positive reaction
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 \(\Rightarrow\) lower entry barrier
  \(\Rightarrow\) fast Time-To-Market!
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

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Lignocellulosic Biomass to Fuels Via Pyrolysis

- Stabilization
  - Pyrolysis
  - Deoxygenate
  - Other Refinery Processes

Collaboration with DOE, NREL, PNNL
JV with Ensyn
Commercialization Plan

Biomass

'Green' Electricity

Fuel Oil

Heating Oil

Marine Fuels

Transport

Timeline

2008

2009

2011

Stage 1 Upgrader

Stage 2 Upgrader

Pyrolysis Unit

Available Now

Corn Stover

Mixed Woods

Rolling Deployment
Biofuel Production Alternatives

**Lignocellulose**
- Dissolution
- Gasification to “syngas” (CO + H₂)
- Pyrolysis, fast or slow

**Sugar/Starch**
- Corn grain
- Starch
- Saccharification
- Sugar
- Fermentation

**Lipids**
- Algae
- Soy beans
- Transesterification
- Biodiesel

**Jet Fuel**
- Fisher-Tropsch
- Methanol

**Diesel**
- Bio-oil

**Gasoline**
- Butanol
- Ethanol

**Heat/Power**
- Lignin

**Thermal Routes**
- Catalytic routes
- Biological routes
- Synthetic biology
Jim Dumesic: Carbohydrates to Fuels

Carbohydrates

- Ethanol/Butanol
- DMF

Fermentation
- dehydration/hydrodeoxygenation

Oxygenated Intermediates

- ketones/aldehydes
- furfural compounds

Synthesis Gas (H₂:CO)
- Fischer-Tropsch synthesis
- reforming+FT synthesis

Oxygenated Fuels

- Ethers

Alkane Fuels

- C₁ methane
- C₂⁻C₄ LPG
- C₅⁻C₁₂ gasoline
- C₉⁻C₁₆ jet fuel
- C₁₀⁻C₂₀ diesel fuel
- >C₂₀ wax

Jim Dumesic:
Carbohydrates to Fuels

- aqueous phase reforming
- targeted alkane synthesis

alkane synthesis

aqueous phase reforming

1. C-C coupling
2. hydrogenation
3. dehydration/hydrogenation

Oxygenated Intermediates

- H₂:CO₂ (process-H₂)
Virent Energy Systems Overview

- 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

- Note self-separation from water (eliminates energy-intensive distillation)
- Uses 30 – 50 wt% sugar solutions
- Process is water-positive
Combined H₂ and Alkane Production

\[ \text{C}_6\text{O}_6\text{H}_{12} + 6 \text{H}_2\text{O} \rightarrow 6 \text{CO}_2 + 12 \text{H}_2 \]  
Aqueous Phase Reforming

\[ \text{C}_6\text{O}_6\text{H}_{12} + 7 \text{H}_2 \rightarrow \text{C}_6\text{H}_{14} + 6 \text{H}_2\text{O} \]  
Dehydration/Hydrogenation

Combined reaction

\[ 1.6 \text{C}_6\text{O}_6\text{H}_{12} \rightarrow \text{C}_6\text{H}_{14} + 3.5 \text{CO}_2 + 2.5 \text{H}_2\text{O} \]

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

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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Heat/Power
- Synthesis biology
- Catalytic routes
- Biological routes
- Thermal routes
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
Renewable Petroleum™ Technology

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 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.
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 highlevels with other petroleum fuels, and to be fully compatible with existing distribution infrastructure, while offering advantages of significantly reduced emissions.
Cellulosic Biofuels: Got Gasoline?

John R. Regalbuto

Most people think of ethanol as "the" liquid biofuel, and that the major advances in biofuels will involve enzymes to convert sugar in corn grains. However, processing biomass into fuels requires breaking down plant tissues into cellulose, hemicellulose, lignin, and other materials. Virent Energy Systems developed a process known as Bio-Forming that converts water-soluble sugars and plastics and pharmaceuticals. Virent Energy Systems developed a process known as Bio-Forming that converts water-soluble sugars and plastics and pharmaceuticals.

Virent – Shell: 100 MM GPY, 2014-2016

Envergent (UOP/Enslyn): 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
Land and Water Use Implications
Next Generation Hydrocarbon Biofuels in the U.S.

- **Land Use**
  - Lignocellulose: no or minimal land use change (Billion Ton Study)
    - Energy crops
    - Forest waste
    - Agricultural residue
  - Algae: grown on marginal land at very high productivity
    - Main issue if economic production
    - Uses existing hydrotreating technology

- **Water Use**
  - Minimized for lignocellulose (residue and drought resistant energy crops)
  - Gasification, pyrolysis, and aqueous phase reforming are water positive
    - Greatly minimize process water vis-à-vis fermentation
    - Will have water treatment issues
  - Hydrocarbon production eliminates distillation
Design needs for hydrocarbon biofuels (workshop)

- Kinetics – Chemkin
- CFD – Fluent
- Thermo/Phase Equilibria - FACT

- R&D
- Process Modeling & Design

- Material & Energy Balance

- Capital & Project Cost Estimates

- Economic Analysis

- Environmental Analysis

- LCA
  - TEAM
  - SimaPro
  - GREET

- General: EXCEL, STELLA (dynamic modeling)

- EXCEL
- Crystal Ball
- At-Risk

- Unscrambler
- MatLab

- ASPEN
- Process Estimator (IPE)

- ASPEN – Icarus

- CFD – Fluent
- Fluent

- ASPEN – FACT
- FACT

- ASPEN – ASPEN
- ASPEN – Icarus
- Icarus

- ASPEN – IPE
- IPE
Current Status of Hydrocarbon Biofuels in U.S.

- 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” FY 09 EFRI topic, $16 MM
  - USDA, DOD, etc.
## Process Design Needs

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Potential advantages of hydrocarbons

- Self-separation from water - no distillation required. Less energy input:
  - lowers processing cost
  - improves the C footprint

- ~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