Next Generation Hydrocarbon Biorefineries

National Academy Workshop:
Expanding Biofuel Production

Madison, WI

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National Science Foundation

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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 → 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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The Solution:

- Produce hydrocarbons from lignocellulose grown with minimal land use change
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

\[ \text{NO} + \text{CO} \rightarrow \text{N}_2 + \text{CO}_2 \]

Pt/Rh/Al₂O₃ catalyst

washcoat
Catalysts: Heart of Petroleum Refineries
Fuels, Chemicals, Materials (Textiles)
Biofuel Production Alternatives

Gasification to "syngas" (CO + H₂)

Pyrolysis, fast or slow

Dissolution

Liquid phase processing

Fisher-Tropsch

Gasoline

Ethanol

Jet Fuel

Diesel

Gasoline

Ethanol

Biodiesel

Heat/Power

Lignocellulose

Sugar/Starch

Lipids

Sugarcane

Corn grain

Switchgrass

Corn stover

Forest waste

Dissolution

Saccharification

Fermentation

Hydrotreating

Transesterification

Fisher-Tropsch

Methanol

Butanol

Synthetic biology

Catalytic routes

Biological routes

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

- Power Generation Module (Genset)
- Gas Production Module
- Biomass
- Feedstocks:
  - Wood chips
  - Ag residues
  - Cubes & Pellets
  - Nut shells
  - Cardboard
  - Paper
  - Etc.

25 Gallons of Syndiesel / Day
Per 0.5 Tons of Biomass

Community Power Corporation
The Modular Bioenergy Company
Biofuel Production Alternatives

gasification to “syngas” (CO + H₂)
pyrolysis, fast or slow
saccharification
fermentation
hydrotreating
transesterification
methanol
bio-oil
Lignin → Heat/Power

Jet Fuel
Diesel
Gasoline
Ethanol
butanol

Forest waste
Corn stover
Switchgrass
Sugar/Starch
Corn grain
Sugarcane
Lipids
Alga
Soybeans
Biodiesel

Fisher-Tropsch
thermal routes
catalytic routes
biological routes
synthetic biology
Gasoline from Cellulose by Catalytic Fast Pyrolysis in a Single Reactor

Cellulose → Pyrolysis to Sugars, Adsorption into catalyst → Glucose in ZSM-5 → Catalytic Conversion → Gasoline, CO₂, Water
BCC = **Biomass Catalytic Cracking**

![Diagram of biomass catalytic cracking process](image-url)
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!
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

Corn Stover

Mixed Woods

Biomass → Pyrolysis → Stabilization → Biocrude → Deoxygenate

- Gasoline
- Diesel
- Jet
- Chemicals

Other Refinery Processes

Collaboration with DOE, NREL, PNNL
JV with Ensyn
Envergent’s Commercialization Plan

- Biomass
  - Corn Stover
  - Mixed Woods

Pyrolysis Unit

- ‘Green’ Electricity
- Fuel Oil
- Heating Oil
- Marine Fuels
- Transport Fuels

Stage 1 Upgrader
Stage 2 Upgrader

Timeline

- 2008
- 2009
- 2011

Available Now

Rolling Deployment
Biofuel Production Alternatives

- Gasification to “syngas” (CO + H₂)
- Pyrolysis, fast or slow
- Liquid phase processing
- Saccharification
- Fermentation
- Transesterification
- Hydrotreating
- Heat/Power
- Biodiesel
- Jet Fuel
- Diesel
- Gasoline
- Ethanol
- Butanol
- Methanol

Feedstocks:
- Forest waste
- Corn stover
- Switchgrass
- Sugar/starch
- Corn grain
- Sugarcane
- Lipids
- Alga
- Soybeans
- Synthetic biology
- Catalytic routes
- Thermal routes
- Biological routes
**Oxygenated Fuels**

- Ethanol/Butanol
- DMF

**Jim Dumesic: Carbohydrates to Fuels**

- **Carbohydrates**
  - fermentation
  - dehydration/hydrodeoxygenation
  - gasification
  - aqueous phase reforming

- **Synthesis Gas** (H₂:CO)
  - ketones/aldehydes
  - furfural compounds

- **Oxygenated Intermediates**
  - H₂:CO₂ (process-H₂)

- **Oxygenated Fuels**
  - Ethers

- **Alkane Fuels**
  - C₁ methane
  - C₂-C₄ LPG
  - C₅-C₆ gasoline
  - C₉-C₁₆ jet fuel
  - C₁₀-C₂₀ diesel fuel
  - >C₂₀ wax

- **Reforming + FT synthesis**
  - targeted alkane synthesis
  - 1. C-C coupling
  - 2. hydrogenation
  - 3. dehydration/hydrogenation
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
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
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
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”**
  - Utilize existing corn EtOH plants for blending at E10 (15 billion gal/yr)
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- **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 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

- 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)
Combined \( H_2 \) and Alkane Production

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

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

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.

Microchannel Fischer-Tropsch Reactor Concept

Close integration of the exothermic Fischer-Tropsch synthesis and steam generation
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: \((C_6H_{10}O_5)_n \rightarrow \text{Gases} + \text{VOC} + \text{Char}\)
Char + O\(_2\) \rightarrow \text{Gases}

Oxidation: \(\text{VOC} + O_2 \rightarrow \text{Gases}\)

Reforming: \(\text{VOC} + H_2O \rightarrow \text{Gases}\)
\(\text{CO} + H_2O \leftrightarrow \text{CO}_2 + H_2\)

Global Chemistry:
\((C_6H_{10}O_5)_n + O_2 + H_2O \rightarrow \text{CO} + \text{CO}_2 + H_2 + H_2O\)

Reactor

Fuel + O\(_2\) + Co-feed

Heat

Generation
Conduction
Convection

Endothermic
Exothermic
Endothermic

Synthesis Gas
CPOx of Cellulose w/ Steam

Biomass

Drying/Grinding/Pretreatment

One-Step Catalytic Gasification

Synthesis

Power

Fuel Separation

www.engr.wisc.edu/che/
Aromatic Selectivity

- Glucose
- Cellobiose
- Cellulose
- Xylitol

Selectivity (%)

- Benzene
- Toluene
- Xylenes, Ethyl-benzene
- Methyl-ethyl-benzene, trimethyl-benzene
- Indanes
- Naphthalenes
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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- Transesterification
- Fish-Tropsch
- Methanol
- Bio-oil
- Lignin
- Heat/Power
- Butanol
- Ethanol
- Gasoline
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- Jet Fuel

Materials:
- Forest waste
- Corn stover
- Switchgrass
- Sugar/starch
- Corn grain
- Sugarcane
- Lipids
- Algae
- Soybeans

Processes:
- Thermal routes
- Catalytic routes
- Biological routes
- Synthetic biology
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

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 Biocombustíveis 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