Catalytic Conversion of Lignocellulosic Biomass to Conventional Liquid Fuels and Chemicals

Randy D. Cortright
CTO/Founder

Catalysis and Alternative Feedstocks for the Biofuels Industry
Council for Chemical Research's New Industrial Chemistry and Engineering Workshop

9/31/2011
Virent at a glance

The global leader in catalytic biorefinery research, development, and commercialization

Employees

105 Employees

Financial

> $76 MM in Private Funding
> $61 MM in Gov & Industry

Infrastructure

Partners & Investors

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Strategic Investors & Partners

Feedstock Logistics
- Major Shareholder
- Participating in feedstock development and commercial deployment

Conversion Platform
- Platform Research & Development
- Technology Provider
- Feedstock R&D
- Catalyst Development
- Operations

Deployment Opportunity
- Major Shareholder
- Development Partner
- Fuel Qualification
- Scale-Up Partner
- Market Channels

Customer Acceptance
- Shareholder
- Support Efforts to Determine BioGasoline’s Suitability in Current & Next Generation Engines
Employees from leading energy, agribusiness and chemical companies; start-ups; and research institutes

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The BioForming® Process

Converting Multiple Feedstocks to High Value Hydrocarbons

Familiar to Petrochemical Industry
- Similar Reactor Processing Practices
- Proven Catalytic Scale-Up Engineering
- Industry Experience Operating at Scale

High Quality Drop-in Products
- Premium Hydrocarbon Mixtures
- Tunable to Produce Desired Blends
- Adaptable to Provide Chemicals
- Compatible with Logistics Infrastructure
- High Energy Content

Cellulosic
Sugars
Starches

Aqueous Phase Reforming
Reactive Intermediates
Conventional Chemical Processing

Chemicals
Fuel Gas
Hydrogen
Reformate
Gasoline
Jet
Diesel
BioForming Feedstock Advantage

Sucrose Starch

Cellulose (35-50%)

Hemicellulose (15-35%)

Lignin (15-35%)

Others: 5-15% (Ash, Extractives)

Fermentable Sugars (Glucose)

Hexose (Glucose, Mannose, Galactose)

Pentose (Xylose, Arabinose)

Oligosaccharides

Sugar Degradation (Furfurals, HMF, Organic Acids)

Lignin

Soluble Cyclics & Phenolics

Ash & Soluble Inorganics

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Virent Technology can Replace > 90% of the Barrel

The US consumes over 18 million barrels of oil per day. 49% is imported from foreign countries.
BioForming® Concept

Sugar Cane

Biomass

Corn Starch

APR

ZSM-5

Condensation

Hydrotreating

Gasoline

Diesel

Kerosene

Jet Fuel
Intermediate oxygenate composition impacts downstream processing
Intermediates can be tuned to achieve different final product goals
Reaction of Oxygenates over ZSM-5

- **Isopropyl Alcohol**
  - Hydride Transfer
  - Dehydration
  - $H_2O + \text{Olefin Pool}$

- **Acetone**
  - Aldol Condensation/
    Eneone Cracking
  - Hydride Transfer
  - $H_2O + \text{Aromatics and Paraffins}$

- **Acetic Acid**
  - Ketonization
  - $0.5$+$0.5$+$0.5+CO_2$+$H_2O$+$\text{Ethylene}$

- **Ethanol**
  - Dehydration
  - $\text{Reducing Equivalents}$
Hydrolysates $\rightarrow$ APR $\rightarrow$ ZSM-5 $\rightarrow$ Gasoline, Aromatics
### Product Development Progress

<table>
<thead>
<tr>
<th>Date</th>
<th>Jan-2008</th>
<th>July-2008</th>
<th>Sep-2008</th>
<th>Dec-2008</th>
<th>Apr-2009</th>
<th>Eagle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dienes and Cyclic olefins</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidity</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Ketones</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Distillation End Point</td>
<td></td>
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</tr>
</tbody>
</table>

**Increasing Quality and Volume**
Virent’s BioGasoline Product

Premium product with the same components as petroleum derived gasoline

Unleaded Gasoline
115,000 BTUs/Gal

Bioforming BioGasoline
+120,000 BTUs/Gal

Ethanol
76,000 BTUs/Gal

~ 20 liters of sugar derived gasoline from Virent’s Bioforming process.
• Virent has 20+ continuous and integrated pilot plants
• Contains feed carboy, pumps, heaters, jacketed reactors, cooler, separators
• Automated control allows for 24/7 operation
• Multiple temperature, pressure, & flow measurement points with data collection
• Feed rates range from 0.1 to 40 mL /min
• Plants easily modified to a myriad of process steps and configurations

• Scale-up of 100X
• Full length reactors and commercial scale catalyst
• 10,000 gal/yr sugar to gasoline integrated continuous process plant
• Feedstock handling and purification system flexibility
• Fully automated and controlled by DCS (Delta V)
• Product volumes for registration, fleet testing, and Ferrari Scuderia race team
Virent BioGasoline in Scuderia Ferrari race fuel.
Generation of Hydrocarbons from Sugar with In-situ Hydrogen Generation

- Recovery of bio-based carbon can be increased by suppressing reforming reactions and using externally supplied hydrogen.

**Overall Theoretical Stoichiometry**

\[ 3.58 \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow \text{C}_{14}\text{H}_{30} + 7.5 \text{CO}_2 + 6.5 \text{H}_2\text{O} \]

Hydrocarbon contains 65 % of Sugar Carbon

\[ 2.33 \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow \text{C}_{14}\text{H}_{30} + 14\text{H}_2\text{O} \]

Hydrocarbon contains 100 % of Sugar Carbon

Instead, bring in \( \text{H}_2 \) from external source.
• Natural gas as a supplemental feed can improve economics as a low cost source of hydrogen.
• Internal \( \text{H}_2 \) Production or External Supply
  – Stoichiometry Example
  – \( \text{2.08 C}_6\text{H}_{12}\text{O}_6 = \text{C}_8\text{H}_{18} + 4.5 \text{ CO}_2 + 3.5 \text{ H}_2\text{O} \)
  – \( \text{4 C}_6\text{H}_{12}\text{O}_6 + 27 \text{ H}_2 = 3 \text{ C}_8\text{H}_{18} + 24 \text{ H}_2\text{O} \)

<table>
<thead>
<tr>
<th></th>
<th>Internal H2 (lbs glucose / gal) {lbs glucose/lb HC}</th>
<th>External H2 (lbs glucose / gal) {lbs glucose/lb HC}</th>
<th>Theoretical H2 Requirement (kg H2 /gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane</td>
<td>19.3 {3.3}</td>
<td>12.3 {2.1}</td>
<td>0.42</td>
</tr>
<tr>
<td>Xylene</td>
<td>21.3 {2.9}</td>
<td>16.2 {2.3}</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Process Yield Advantage

Theoretically Achievable Fermentation Hydrocarbon Yield

Specific Feedstock Consumption

- Nov-2008
- Feb-2009
- Jan-2010
- Nov-2010
- Mar-2011

Theoretically Achievable Yield for Catalytic Conversion

Goal
Cash cost break even for a Virent Bioforming refinery producing aromatic chemicals and biogasoline.

Notes:
*Product Values utilize historic Crude to Product Value Ratios from Mid 2007 to Mid 2010
*Major Utilities Cost Assumptions of $6/mmbtu NG and $0.07/kw-hr
*Includes Variable and Fixed costs
Sugars to Cellulosic Migration Plan

CURRENT PROCESS

COMMODITY SUGARS
- Corn Starch
- Sugar Cane
- Sugar Beet

BIOFORMING
Virent’s proprietary process to transform cost-effective sugars into fuels and chemicals

HYDROCARBON PRODUCTS
- Gasoline
- Diesel
- Jet Fuel
- Chemicals
- Plastics

IN DEVELOPMENT

NON-FOOD SUGARS
- Corn Stover
- Bagasse
- Switchgrass
- Miscanthus
- Wood

DECONSTRUCTION TECHNOLOGIES
Liberate sugars from cellulosic biomass cost-effectively

Development Portfolio
National Advanced Biofuel Consortia
HCL Cleantech Collaboration
NREL Collaboration
In-house Technology Development

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Virent Deconstruction Partners

- Dilute acid pretreatment and enzyme hydrolysis
- Wet oxidation and enzyme hydrolysis
- Strong acid pretreatment
- Virent catalytic deconstruction
Recent Developments - Biogasoline

Cellulosic biomass to gasoline, 6/2/2011

© 2011 – Virent, Inc.
Recent Progress - Biogasoline

NABC Work
- Stover from ISU, pine residues from Catchlight
- NREL, WSU, and Virent making Hydrolysates
- Virent converted hydrolysates into BioFormate™ gasoline product
Virent produces a biobased reformate that is identical to petroleum reformate in an oil refinery.

Reformate is used as a high octane blend component in gasoline.

Reformate is a significant source of benzene, toluene, and xylenes used in the chemical industry.

Nearly 70% of the world’s aromatics are derived from reformate.

Shale gas and gasoline market dynamics are reducing the production of reformate from refineries.

Continued upward pricing pressure on aromatics is expected.
Virent’s BioGasoline product resembles a typical refinery reformate stream which is the dominant feedstock source for many chemicals and plastics in use today.

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Typical Catalytic Reformate (Vol%)</th>
<th>Virent BioGasoline Product (Vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paraffins</td>
<td>22.5</td>
<td>20.6</td>
</tr>
<tr>
<td>Napthenes</td>
<td>0.7</td>
<td>3.9</td>
</tr>
<tr>
<td>Aromatics</td>
<td>60.8</td>
<td>64.4</td>
</tr>
<tr>
<td>Overall Totals</td>
<td>84.0</td>
<td>88.9</td>
</tr>
<tr>
<td>Typical RON</td>
<td>~95 - 105</td>
<td>105</td>
</tr>
</tbody>
</table>
Virent enables production of 100% bio-based renewable PET fibers, films and bottles.
Virent Unveils Biobased P-Xylene Process

2:52 PM MDT | June 6, 2011 | Rebecca Coons

Virent (Madison, WI), a catalytic chemistry firm, says it has successfully produced *para*-xylene (*p*-xylene) from plant-based sugars. The *p*-xylene, which Virent has tradenamed BioFormPX, is identical to *p*-xylene produced via petroleum-based processes and can be used as a drop-in replacement in the value chain, says Kieran Furlong, Virent’s commercial manager/chemicals.

The breakthrough will allow polyethylene terephthalate (PET) manufacturers to produce the commodity resin entirely from renewable resources.

Coca-Cola is working to increase the renewable content of its packaging.
Benzene, Toluene and Xylenes have a wide range of everyday end use products and are heavily dependent on fossil fuel sources for production.
Current State-of-the-Art PET

Existing technology for the production of bio-MEG enables a partially bio-based PET bottle (up to 30%)

Adapted from Coca-Cola website graphic
http://www.thecoca-colacompany.com/citizenship/plantbottle_basics.html
Virent technology for bio-based PX enables a 100% bio-based PET bottle that is:

- 100% Recyclable
- 100% Renewable

Adapted from Coca-Cola website graphic
http://www.thecoca-colacompany.com/citizenship/plantbottle_basics.html
Renewable Jet Fuel

Jet Range Aromatics

Other Hydrocarbons
Paraffins
Aromatics

Jet A Fuel
Virent Jet Fuel

ASTM
Virent
Density (kg/m³) 775 to 840 780
Freeze Point (°C) <47 <74
Sulfur (wt%) <0.3 <0.01
BioForming® Concept

- **Biomass**
- **Sugar Cane**
- **Corn**

**APR**

- Modified ZSM-5
- Condensation + Hydrotreating

**Reformate**

- Aromatics
  - Gasoline
  - Diesel

**Optionality for jet aromatics**

- **Distillate**
  - Jet Fuel
  - Diesel

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Fully Renewable Synthetic Jet

Polarity

Boiling Point

85% RPN + 15% ARJB
Excellent freeze point and density due to unique Virent jet composition

Virent D-86 comparison to Jet-A

High thermal stability ensures low levels of impurities

<table>
<thead>
<tr>
<th>Specification Test</th>
<th>MIL-DTL-83133G Spec Requirement</th>
<th>JP-8</th>
<th>VIRENT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical and Chemical Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of Combustion (measured), MJ/Kg</td>
<td>≥42.8</td>
<td>43.3</td>
<td>43.3</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>≥38</td>
<td>51</td>
<td>40</td>
</tr>
<tr>
<td>Freeze Point, °C</td>
<td>≤-47</td>
<td>-50</td>
<td>&lt; -60</td>
</tr>
<tr>
<td>Density @ 15°C, kg/L</td>
<td>0.775 - 0.840</td>
<td>0.804</td>
<td>0.805</td>
</tr>
<tr>
<td><strong>Distillation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% recovered ($T_{10}$), °C</td>
<td>≤205</td>
<td>182</td>
<td>164</td>
</tr>
<tr>
<td>EP, °C</td>
<td>≤300</td>
<td>265</td>
<td>290</td>
</tr>
<tr>
<td>$T_{90}-T_{10}$, °C</td>
<td>≥22</td>
<td>62</td>
<td>86</td>
</tr>
<tr>
<td><strong>Thermal Stability</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>260°C</td>
<td>325°C</td>
<td></td>
</tr>
<tr>
<td>Tube Deposit Rating</td>
<td>&lt;3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Change in Pressure, mm Hg</td>
<td>≤25</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>
U.S. Market Potential Vs. Feedstock Cost
Projected Feedstock Availability in 2022

Points represent ranges in feedstock prices less co-products from January 2006 to present. Data taken from USDA, IMF, and DOE Billion Ton Study Update.

Crop prices are considered wholesale prices while Biomass price is “roadside” or “farmgate” price and does not include any storage or transportation costs.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Contribution to Manufactured Fuel Cost ($/Gal of Fuel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US Corn Crop</td>
<td>$3.12/bu &quot;net oil&quot; ($9.05/bu soybeans)</td>
</tr>
<tr>
<td>US Soybeans Crop</td>
<td>$100/ton</td>
</tr>
<tr>
<td>US Biomass</td>
<td>$40/ton</td>
</tr>
</tbody>
</table>

2010 U.S. Production of Jet Fuel

Potential Fuel Production (Billion Gallons per Year)
Recent Developments – Jet Fuel Award

DOE Award
- Announced June 10, 2011
- Cellulosic sugars to jet fuel
- $13.4 MM Grant
- 3 year project

Project Partners
- Jet fuel production
- Corn stover processing
- Modeling
Conventional Diesel GC-GC Analysis

Boiling Point (Carbon Number)

Polarity (Component Class)

2+ Ring Aromatics
1 Ring Aromatics
1,2 Ring Naphthenes
Paraffins
FAME

Road Diesel
Paraffins
1,2 Ring Naphthenes
1 Ring Aromatics
2+ Ring Aromatics

GC-GC Analysis

Conventional Diesel

GC
## Contribution of Component Classes to Diesel Performance

<table>
<thead>
<tr>
<th></th>
<th>$n$-Paraffins</th>
<th>$i$-paraffins</th>
<th>Naphthenes</th>
<th>Aromatics*</th>
<th>FAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Flow</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Cetane</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Density</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Volumetric Heating Value</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Energy Content</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Broad component range mixtures and classifications to meet current diesel specifications

*Polynuclear aromatics increase particulate emissions

Adapted from “Diesel Fuels Technical Review” available from Chevron
Virent’s Renewable Diesel Properties

Virent’s Renewable Diesel
Aromatics by HPLC – 8.6%
Derived Cetane 45
Cloud Point ≤-60°C
Virent Diesel GC-GC Analysis

Boiling Point
(Carbon Number)

Polarity
(Component Class)

Virent Diesel
### Virent Diesel Specification Compliance

<table>
<thead>
<tr>
<th></th>
<th>ASTM D975 #2 Diesel</th>
<th>EN 590</th>
<th>Virent Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloud Point</td>
<td>Varies</td>
<td>Varies</td>
<td>&lt; -60°C</td>
</tr>
<tr>
<td>Flash Point</td>
<td>&gt; 52</td>
<td>&gt; 55</td>
<td>56°C</td>
</tr>
<tr>
<td>Cetane</td>
<td>&gt; 40</td>
<td>&gt; 51</td>
<td>45</td>
</tr>
<tr>
<td>T95</td>
<td></td>
<td>&lt; 360</td>
<td>&lt; 340°C</td>
</tr>
<tr>
<td>Density</td>
<td>-</td>
<td>820-845 Kg/m³</td>
<td>Conforming</td>
</tr>
</tbody>
</table>

- Inherently excellent cold flow properties
- High blend potential
- No PNAs ➔ expected low PM emissions
- Cetane can be increased through operational controls
IF YOU CAN GROW IT,
we can convert it into everyday fuels, plastics and chemicals.

Virent is replacing crude oil. Visit our website to learn how.