Catalytic Conversion of Carbohydrates to Hydrocarbons

DOE Biomass R&D TAC Meeting

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Paul Blommel, PhD
Director of Process Chemistry, Virent Energy Systems, Inc.
BioFuel Pathways from Biomass

- Biomass
  - Conversion of Carbohydrates to Hydrocarbons
    - Hydrolysis
      - Sugars
        - Aqueous Phase Reforming
          - Ethanol
          - Butanol
          - Hydrocarbons
        - Fermentation
          - Ethanol
          - Methanol Ethanol
        - Refining
          - Liquid Fuels
    - Pyrolysis
      - Bio-oils
        - Syngas
          - Gasification
            - CO + H₂

- Fischer-Tropsch
  - Diesel
  - Jet Fuel
Overall Theoretical Stoichiometry with *in situ* hydrogen generation

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

Hydrocarbon contains 65% of Sugar Carbon

Hydrocarbon contains 94% of LHV of Sugar

*Potential LHV of liquid fuel product/LHV of carbohydrate feed*
A catalytic route to renewable hydrocarbon fuels and chemicals.

- Feedstock Flexible
  - Conventional Sugars
  - Non-Food Sugars
- Drop-in Products
  - Liquid Fuels and Chemicals
  - Tunable Platform
  - Infrastructure Compatible
- Fast and Robust
  - Inorganic Catalysts
  - Moderate Conditions
  - Low Residence Times
- Energy Efficient
  - Exothermic
  - Low Energy Separation
BioForming® Platforms

Sugar Cane

Biomass

Corn Starch

Aromatics and Paraffins

Gasoline + Aromatics

Kerosene

Jet Fuel

Diesel

Modified ZSM-5

Reactive Intermediates

Condensation

Hydrotreating

APR
Generation of Reactive Intermediates

Reforming

\[ \text{R} \text{OH} + \text{H}_2\text{O} \rightarrow \text{R}_2 \text{H}_2 + \text{CO}_2 \]

Deoxygenation

\[ \text{R}_2 \text{OH} \rightarrow \text{R}_2 \text{H} + \text{H}_2\text{O} \]

**APR Reactants**

- Xylose Oligomers
- HMF
- Xylose
- Glucose
- Levulinic Acid
- Cellulose Oligomers
- Benzene

**Combined Reforming and Deoxygenation**

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{R}_2 \text{OH} \]

\[ \text{R}_2 \text{OH} + \text{H}_2\text{O} \rightarrow \text{R}_2 \text{H}_2 \]

**APR Products**

- Carboxylic Acids
- Esters
- Alcohols

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**C₅ & C₆ Sugars**

- Hydrolysates

\[ \text{Hydrolysates} \rightarrow \text{APR} \rightarrow \text{Catalytic Conversion} \rightarrow \text{Fractionation} \rightarrow \text{Gasoline Product} \]
Production of Hydrocarbons from Reactive Intermediates

- **Isopropyl Alcohol**
  - Hydride Transfer
  - Dehydration
  - Propylene
  - Reducing Equivalents

- **Acetone**
  - Aldol Condensation/Enone Cracking
  - Ketonization
  - Hydride Transfer
  - Acetaldehyde
  - Ethanol

- **Acetic Acid**
  - Hydride Transfer
  - Dehydration

- **C5 & C6 Sugars**
  - Hydrolysates
  - APR
  - Catalytic Conversion
  - Fractionation
  - Gasoline Product

- **Olefin Pool**
  - Aromatics and Paraffins
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.
Catalytic Processing Offers Flexibility to Replace More than Fuels

Bio-reformate can replace typical reformate which is dominant feedstock for many chemicals, fibers, and plastics in use today.

- Benzene
- Toluene
- Para-Xylene
- Meta-Xylene
- Ortho-Xylene

**Product Composition Flexibility**
Process Scale Up – Gasoline/Aromatics

- Carbohydrates-to-Aromatics process
- Scale-up of x100 from pilot plant
- 10,000 gallons per year
- Full Length Reactor and Commercial Scale Catalyst
- Product volumes for registration and fleet testing
- Feedstock handling and purification system flexibility
- Operations started in November 2009
- Overall success: On time, under budget, high quality product
BioForming® Platform - RPN

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

**APR**
- Condensation
- Hydrotreating

**Modified ZSM-5**

**Paraffins and Naphthenes**

- **Gasoline + Aromatics**
- **Kerosene**
- **Jet Fuel**
- **Diesel**

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Virent RPN Characteristics

**Boiling Point**

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<th>Max Jet</th>
<th>Max Diesel</th>
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<tr>
<td>Gasoline</td>
<td>20%</td>
<td>20%</td>
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<tr>
<td>Jet</td>
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<tr>
<td>Diesel</td>
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<td>60%</td>
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<tr>
<td>Process Oil</td>
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- **Flexible product slate**
- **Product is uniquely advantaged due to both component classes and ability to meet broad boiling point specifications**
- **Jet certification challenging and requires large volumes**
Feedstock flexibility for catalytic conversion

Biomass

- Cellulose (35-50%)
- Hemicellulose (15-35%)
- Lignin (15-35%)
- Others: 5-15% (Ash, Extractives)

Monosaccharides

- Hexose (Glucose, Mannose, Galactose)
- Pentose (Xylose, Arabinose)

Oligosaccharides

Sugar Degradation (Furfurals, HMF, Organic Acids)

- Lignin
- Soluble Cyclics & Phenolics
- Ash & Soluble Inorganics

Catalytic Routes vs. Microbial Conversion
Virent leads the Catalytic Conversion of Lignocellulosic Sugars (CLS) strategy. The underlined parties above are currently collaborating within the CLS strategy.
• Dilute acid pretreatment and enzyme hydrolysis

• Wet oxidation and enzyme hydrolysis

• Strong acid pretreatment

• Virent catalytic deconstruction
Catalytic Lignin Conversion

**Traditional Approach to Lignin Hydrotreating**
Removal of Phenols is Challenging

2-methoxy-phenol

**Virent’s Upgrading Approach**
PtRe/Al2O3
Pt/L. Zeolite
Pt/ZSM-5
IF YOU CAN GROW IT,
we can convert it into everyday fuels, plastics and chemicals.