Maizeoline: Biomass to Diesel via Furfural

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What is Biodiesel

- Biodiesel is a renewable, clean burning fuel made from plant-based products
Importance

1. 6.57 billion barrels of petroleum products consumed in the US in 2013
2. ~18 million barrels/day
3. Import ~ 9.3 million barrels/day as of 2014 from 80 different countries
4. Eventually all known reserves will be depleted
Applications and Uses for Biodiesel

- Can be used in all diesel engines.
  - Cleans out engines
  - Lubricates better than petro-diesel
- Was licensed by the California Department of Fish and Game as a shoreline cleaning agent.
- Paint and adhesive remover
Advantages of Biodiesel

- Renewable feedstock
- Meets the Clean Air Act Amendments
- Comparable energy density and energy content to petro-diesel
- Compatible with existing engines
- Biodegradable
Properties of Biodiesel

- Immiscible with water
- High flash point
- Low vapor pressure
Location and Market Opportunities

- Plant Location: Spencer, Iowa
- Fairly new technology that is being looked by several different companies
- Can be blended with petro-diesel
- Consumers
  - US Military
  - Disneyland
  - National Parks
Approximate Yield from Corn Stover (Mass Percent)

5.5% mass of Corn Stover can be converted into Diesel
Biomass Hydrolysis, Dehydration to Furfural

Ethanol Plant

Ethanol

Furfural Hydrogenation to 2-Methyl Furan

Power Plant

Electricity

2-Methyl Furan Alkylation to C15 Ketone

C15 Ketone Hydrodeoxygenation to Diesel

Bio-Diesel
Biomass to Furfural

- Corn Stover

  Biomass Grinding

  Sulfuric acid

  Furfural Generation

  Unused Biomass

  Ethanol Plant

  O-nitrotoluene

  Furfural Separation

  Wastewater

  Furfural
Furfural Generation

- MTC is a novel reactor designed at Delft University of Technology to minimize by-products and improve yield.

- Only significant by product is acetic acid
- **72.7% yield** (mass basis)
Furfural Separation

- NaOH neutralizes the sulfuric acid and generates sodium sulfate ions
- O-nitrotoluene is used to remove most of the water in the extraction tower.
- Sodium sulfate ions compete with furfural for hydration → improved furfural separation from water
- Two vacuum distillation towers isolate furfural from the organic solvent and residual water.
Ethanol Production Summary

- Recombinant strain of *Zymomonas mobilis* ferments glucose and pentose sugars into ethanol and $\text{CO}_2$

  $\text{C}_6\text{H}_{12}\text{O}_6\text{(aq)} \rightarrow 2\text{CH}_3\text{CH}_2\text{OH}\text{(aq)} + 2\text{CO}_2\text{(g)}$

- Recovered as a 99.5% ethanol product
- ~150,000 lb/hr is produced
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Electricity
Furfural to 2-MethylFuran

Flowchart:
- Furfural enters the Reactor
- Hydrogen enters the Reactor
- Furfural and Hydrogen react in the Reactor
- 2-MethylFuran exits the Separation/Purification
- Furfural enters the Separation/Purification
- Waste Water exits the Separation/Purification
- Furfuryl Alcohol exits the Separation/Purification
- Hydrogen exits the Reactor and enters the Power Plant
- Vent exits the Separation/Purification
Reactor

- Exothermic Hydrogenation Reaction
- Catalyst: Copper Chromite on Activated Charcoal
- Temperature: 195-205 °C
- Pressure: 1atm
- 53.3% Yield
Separation Process

- Flash Drum
  - Separate Hydrogen from affluent of reactor
- Series of 3 Distillation Columns
  - 1 Vapor Liquid Liquid Column
  - 2 for Furfuryl Alcohol Purification
2-Methylfuran Alkylation to C15 Ketone

Reactors

Separation: Decanter

2-Methylfuran

Water

C15 Ketone

Water

Water Recycle
2-Methylfuran Alkylation to C15 Ketone

\[ 3 \text{H}_3\text{C} - \text{O} \quad + \quad \text{H}_2\text{O} \quad \rightarrow \quad \text{5,5-bisilyl-2-pentanone (C}_{15}\text{H}_{18}\text{O}_3) \]

Water Is Not Consumed
2-Methylnfuran Alkylation to C15 Ketone

- Packed Bed Reactor
- 60°C and Atmospheric Pressure
- Catalyst: ITQ-2 delaminated zeolite
- C15 Ketone = 5,5-bisylvyl-2-pentanone
- 94% Yield
Block Diagram

Biomass Hydrolysis, Dehydration to Furfural

Ethanol Plant

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Bio-Diesel
C15 Ketone Hydrodeoxygenation to Diesel

C15 Ketone

Heat Exchanger

Reactor

Separation: Decanter

Separation: Distillation

C15 Ketone

Hydrogen

Diesel

Byproducts

Water

Vent

Overhead

Diesel

Organic Phase
C15 Ketone Hydrodeoxygenation to Diesel

- Packed Bed Reactor
  - 350°C and 5 MPa
  - Catalyst: Platinum on Active Carbon
- 92.6% Yield

![Chemical structures](image)
Byproducts

- From Decanter:
  - Dirty Water
  - Vented Hydrocarbons

- From Distillation:
  - Gaseous Hydrocarbons

Hydrocarbons = $C_1$ to $C_8$ Range

- Propane = $C_1$ to $C_4$ Representative
- n-Hexane = $C_5$ to $C_8$ Representative
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Ethanol

Electricity

Bio-Diesel

Power Plant

Ethanol Plant
Power Plant

- $66 MM Capital Investment
- Capture 80% of Firing Duty for Steam
  - 1.6 MM lb/hr Generated (540°C, 600 psia)
- 85% Efficient Turbines
  - 180°C, 145 psia Steam Sent to the MTC
- 81 MW of Electricity Generated
- 40 MW to the Grid
Aspen Modeling Properties

- NRTL Property Method
- Joback
  - Pure Component Estimation
    - $T_c$, $P_c$, $T_B$, $V_c$, $Z_c$, and DHFORM
- UNIFAC
  - Estimate Missing Activity Coefficients
Waste Water Treatment

- Ames Water Pollution Control Facility
  - Uses physical and biological treatment methods
  - Remove organic materials, solids, ammonia, and meet oxygen demand before discharging to Skunk River
- Include a Non-Domestic Waste Pretreatment Program
- Total wastewater cost: $12.26 MM per year
Feed Stock Analysis

- Corn Stover required to meet Biodiesel requirement
  - 7.491 Billion lb/year
    - Will need approximately 5.853 million bales/year
    - Area required: ~ 1 million acres
- Corn Production in Iowa
  - 13.7 million acres
Costs

- Catalysts and Capital costs are a one time cost.
- Yearly cost averages $312.6 MM$

<table>
<thead>
<tr>
<th>Cost Description</th>
<th>Total Cost MM$</th>
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<tbody>
<tr>
<td>Feed Streams</td>
<td>$300.3</td>
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<tr>
<td>Capital Cost</td>
<td>$163.9</td>
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<td>Waste water</td>
<td>$12.3</td>
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<tr>
<td>Catalysts</td>
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<tr>
<td><strong>Total Cost</strong></td>
<td><strong>$485.0</strong></td>
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## Revenue/ Profits

<table>
<thead>
<tr>
<th>Description</th>
<th>Yearly Profits MM$</th>
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<tbody>
<tr>
<td>Ethanol</td>
<td>$470.8</td>
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<tr>
<td>Furfuryl Alcohol</td>
<td>$385.9</td>
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<tr>
<td>Biodiesel</td>
<td>$209.9</td>
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<tr>
<td>Electricity Credit</td>
<td>$22.04</td>
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<tr>
<td><strong>Total Revenue</strong></td>
<td><strong>$1,088.7</strong></td>
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By-products are the most profitable.
Profitability Analysis

This process is not very sensitive to changes in interest rates

<table>
<thead>
<tr>
<th>Summary</th>
<th>NPV0</th>
<th>$7.23 MMM$</th>
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<tbody>
<tr>
<td>IRR</td>
<td>32%</td>
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<td>Pay Back Period</td>
<td>~3.0 years</td>
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<td>NPV10</td>
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<tr>
<td>IRR</td>
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<tr>
<td>Pay Back Period</td>
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<td>NPV12</td>
<td>$1.91 MMM$</td>
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<tr>
<td>IRR</td>
<td>17%</td>
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<tr>
<td>Pay Back Period</td>
<td>~3.95 years</td>
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Conclusion

Feed:
- 900,000 lb/hr Corn Stover

Production:
- 50,000 lb/hr Biodiesel
- 52,000 lb/hr Furfuryl Alcohol
- 150,000 lb/hr Ethanol
- 40 MW Electricity

Profits:
- 1,088 MM$/year
- Pay Back Period: 3.7 years
- IRR: 19%

This plant is profitable
Acknowledgements

- John Myers
- Joseph Holles
- David Bell
- BP Energy Bioscience Institute, Berkeley, CA


References