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Project Goals and Objectives

- Develop a cost effective route for converting biomass to transportation fuels by
  - Converting biomass to hydropyrolysis oil
  - Upgrading the hydropyrolysis oil in a petroleum refinery using existing refinery equipment
  - Working closely with a major petroleum refining company to develop the best integration
  - Developing a preliminary engineering design for a hydropyrolysis pilot and commercial scale facility to be located next to a Valero refinery
  - Developing an engineering design package for locating a hydropyrolysis unit converting cornstover at one of Valero’s 10 midwest corn ethanol plants
  - Comparing risk versus benefits from a refiners point of view for Integrated hydropyrolysis and hydroconversion (IH²) vs hydropyrolysis plus refinery upgrading

Selected from FOA DE-FOA-0000686 Bio-Oil Stabilization and Commoditization
Project Quad Chart Overview

Timeline
• Jan 2013
• April 2016
• 8.7% spent – project just started

Barriers
• Barriers addressed
  – Pyrolysis of Biomass and Bio-Oil Stabilization

Budget
• Total $4.1MM, $3.2MM DOE, $.88MM CS
• 2013 to date $356K, $280K DOE, $74K CS
• 3 years funding, $1.4MM/year

Partners & Roles
• GTI, CRI Catalyst, Valero, Johnson Timber, Cargill, MTU
Refinery Upgrading of Hydropyrolysis Oil

PROJECT TEAM

- GTI
  - Produce Hydropyrolysis Oil

- CRI- Catalyst
  - Upgrading Tests on Hydropyrolysis Oil

- Valero
  - Refining
  - Refinery Upgrading Analysis, Risk Analysis

- MTU
  - LCA

- Cargill
  - Cornstover Logistics

- Johnson
  - Timber
  - Wood Logistics

• Currently finalizing contracts with partners
U.S. Timber Production by County (2007)

Board feet per hectare

- Less than 0.2
- 0.6 - 1.0
- 1.1 - 1.6
- 1.7 - 2.3
- 2.4 - 3.3
- 3.4 - 4.9
- 5.0 - 10.9

Sources: WRI analysis on national timber production (Johnson et al., 2009), administrative boundaries (ESRI Data and Maps 9.3.1, ESRI, 2008).

▲ Valero Refineries
Adjacent Hydropyrolysis Integration With a Refinery

New Hydropyrolysis

- Best Integration system depends on Oil Refinery specifics-Hydropyrolysis products have low TAN’s and can be blended into Refinery streams – Capital cost could be <$50MM for 2000 t/d of biomass feed

Hydropyrolysis

- Hydrogen (H2)

biodiesel

H2

char

biodiesel

Hydropyrolysis

- Integration of H2 Plant

biodiesel

Hydropyrolysis

- Diesel to H2

biodiesel

Hydropyrolysis

- Gasoline to upgrading

biodiesel
Distributed Hydropyrolysis Sites Feeding an Existing Refinery

Multiple Hydropyrolysis Sites Integrated with Corn Ethanol Production

Hydropyrolysis products sent for further upgrading in existing refinery hydrotreaters
## Advantages of Hydropyrolysis Oil versus Pyrolysis Oil

<table>
<thead>
<tr>
<th></th>
<th>Hydropyrolysis Oil from small batch tests</th>
<th>Pyrolysis Oil</th>
<th>Typical Partially Upgraded Pyrolysis Oil</th>
<th>Typical Catalytic Pyrolysis Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Oxygen</td>
<td>&lt;3</td>
<td>50</td>
<td>8-10</td>
<td>6-10</td>
</tr>
<tr>
<td>% Water</td>
<td>&lt;0.5</td>
<td>20</td>
<td>2-3</td>
<td>2-3</td>
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<tr>
<td>Molecular weight</td>
<td>150-200</td>
<td>500-750</td>
<td>na</td>
<td>na</td>
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<tr>
<td>TAN</td>
<td>&lt;2</td>
<td>100</td>
<td>5-20</td>
<td>5-20</td>
</tr>
</tbody>
</table>

- A more upgraded bio-oil fits in refineries better and presents less risk
Integrated Hydropyrolysis and Hydroconversion (IH$^2$)

- Directly make desired products
- Run all steps at moderate hydrogen pressure (200-500 psi)
- Utilize C$_1$-C$_3$ gas to make all hydrogen required
- Avoid making “bad stuff” made in pyrolysis – PNA, free radicals
Integrated Hydropyrolysis and Reformer System
# Upgrading Hydropyrolysis Oil In a Refinery

<table>
<thead>
<tr>
<th>ID</th>
<th>Task Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FEEDSTOCK PROCUREMENT</td>
</tr>
<tr>
<td>2</td>
<td>Prepare Hydropyrolysis Oil</td>
</tr>
<tr>
<td>3</td>
<td>Restart Plant</td>
</tr>
<tr>
<td>4</td>
<td>Prepare 25 L of Hydropyrolysis Oil from wood</td>
</tr>
<tr>
<td>5</td>
<td>Prepare 25 L of Hydropyrolysis Oil from cornstover</td>
</tr>
<tr>
<td>6</td>
<td>Prepare 25 L of IH2 oil from wood</td>
</tr>
<tr>
<td>7</td>
<td>Prepare 25 L of IH2 oil from cornstover</td>
</tr>
<tr>
<td>8</td>
<td>HYDROPYROLYSIS OIL PREPARED</td>
</tr>
<tr>
<td>9</td>
<td>Fractionate diesel and Gasoline cuts</td>
</tr>
<tr>
<td>10</td>
<td>Hydrotreat oils</td>
</tr>
<tr>
<td>11</td>
<td>Hydrotreat diesel cut from Hydropyrolysis oil from wood</td>
</tr>
<tr>
<td>12</td>
<td>Hydrotreat diesel cut from hydropyrolysis oil from cornstover</td>
</tr>
<tr>
<td>13</td>
<td>Hydrotreat gasoline cut from hydropyrolysis oil from wood</td>
</tr>
<tr>
<td>14</td>
<td>Hydrotreat gasoline cut from hydropyrolysis oil from wood</td>
</tr>
<tr>
<td>15</td>
<td>Hydrotreat diesel cut for IH2 of wood</td>
</tr>
<tr>
<td>16</td>
<td>Hydrotreat diesel cut for IH2 of cornstover</td>
</tr>
<tr>
<td>17</td>
<td>HYDROTREATING COMPLETE</td>
</tr>
<tr>
<td>18</td>
<td>Refinery Integration Analysis</td>
</tr>
<tr>
<td>19</td>
<td>RISK ANALYSIS-OPTIMAL DESIGN REPORT</td>
</tr>
<tr>
<td>20</td>
<td>RIN ANALYSIS</td>
</tr>
<tr>
<td>21</td>
<td>Feedstock Supply Logistics</td>
</tr>
<tr>
<td>22</td>
<td>LCA Analysis</td>
</tr>
<tr>
<td>23</td>
<td>LCA REPORT COMPLETE</td>
</tr>
<tr>
<td>24</td>
<td>Engineering</td>
</tr>
<tr>
<td>25</td>
<td>ENGINEERING DESIGN PACKAGE</td>
</tr>
<tr>
<td>26</td>
<td>Technoeconomic Analysis</td>
</tr>
<tr>
<td>27</td>
<td>Project Management</td>
</tr>
<tr>
<td>28</td>
<td>Final report</td>
</tr>
<tr>
<td>29</td>
<td>FINAL REPORT COMPLETE</td>
</tr>
</tbody>
</table>

![Gantt chart showing project timeline and task dependencies](chart.png)
IH² 50 kg/d Continuous Pilot Plant

• Only Continuous IH² Pilot Plant in the world
Schematic Diagram of Continuous IH\(^2\) Process Unit

- 2 kg/hr of biomass feed
- Continuous char-catalyst separation
- Continuous operation
First stage Hydropyrolysis Liquids have smooth boiling point distribution and are primarily gasoline, jet, and diesel.

- Catalyst A
- Catalyst B
- Jet
- Gasoline
- Diesel

Hydropyrolysis Liquid Boiling Point Distribution
Cumulative Wt. % versus Boiling Temperature

0 10 20 30 40 50 60 70 80 90 100

0 100 200 300 400 500 600

• Temperature, °C

• Cum. Wt%
Average Molecular Weight of 1st Stage Hydropyrolysis Oil compared to Pyrolysis Oil

Molecular Wt of Pyrolysis Oil vs 1st Stage Hydropyrolysis Oil

MW

Aged Py Oil | Fresh Py Oil | HP Cat A | HP Cat B
Advantages of Hydropyrolysis vs Pyrolysis

- **H/C**
  - H/C goes up with hydropyrolysis, down with pyrolysis

- **EHI Effective Hydrogen Index**
  - EHI = (H - 2O - 3N - 2S)/C is a measure of coking, higher EHI = less coking
Conclusions and Future Work

> Project will look at refinery integration to minimize cost for biomass conversion to gasoline and diesel

> Goal is to work closely with Valero and develop the best possible process integration for refiners

> Project also enables study of hydropyrolysis step alone in IH² – very important for hydropyrolysis design

> Project enables continuous testing of hydropyrolysis and IH² for cornstover

> Will gather important comparison of risk for IH² versus hydropyrolysis from a refiners point of view

> Expect excellent LCA and economics of production (estimated <$2/gallon minimum selling cost)

> Remaining work to be done

> Project has just begun so bulk of work remains

> Hydropyrolysis Pilot plant testing to produce hydropyrolysis oil just beginning