Hydrothermal Processing of Wood for Electricity

James Oyler
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Hydrothermal Processing

• Advanced process efficiently converts wet organic matter to biofuels and clean water
  – Can produce bio-crude oil, methane gas, or both
  – App. 99% of organic matter is converted

• Process perfected by US Department of Energy at PNNL over 40-year period with extensive testing

• Process has recently been documented under two major US DOE programs costing USD $100 million
  – NABC for wood
  – NAABB for algae
Terminology and Acronyms

• Hydrothermal Processing = HTP
• Hydrothermal Liquefaction = HTL
• Catalytic Hydrothermal Gasification = CHG
• All of these processes use temperature (350°C) and pressure (200 bar) to convert organic material (biomass or organic chemicals) to hydrocarbon fuels
• Process uses wet materials
  – Must be wet—water is part of reactions
  – Material is processed as slurry with 15% to 30% solids
Avoiding Confusion

• HTP is different than pyrolysis—it is a liquid process, not a dry process
• CHG is not “gasification” as generally used
  – General use almost always means pyrolysis
• Output of pyrolysis is syngas, which is mostly a mix of hydrogen and carbon monoxide
  – Energy content HHV = 280 BTU/scf
• Output of HTP is methane and carbon dioxide
  – Energy content HHV = 620 BTU/scf
Process Concepts

• Process is similar to fossil fuel formation, but faster
  – 30 minutes instead of 30 million years
• Best technology available for converting wet organics to true hydrocarbon fuels (not esters)
• Equipment is compact and scalable
• Tested on more than 100 feedstocks with thousands of hours of runtime
• Liquid fuels refined from the bio-crude are replacements for fossil fuels; methane is methane
  – Gasoline, jet, diesel
## Partial List of Tested Feedstocks

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquatic</td>
<td>Water Hyacinths, Kelp (Marine), Red Algae (Marine), Green Algae (Brackish), Green Algae (Marine), Green Algae (Fresh), Diatoms, Cyanobacteria</td>
</tr>
<tr>
<td>Ligno-Cellulosic</td>
<td>Wood Slash, Sawdust, Corn Stover, Poplar Fermentation Residuals, Wood Gasification Residuals, Cellulosic Fermentation Residuals</td>
</tr>
<tr>
<td>Herbaceous</td>
<td>Napier Grass, Sorghum, Sunflowers, Corn Stover, Marigolds</td>
</tr>
<tr>
<td>Chemical Waste</td>
<td>Nylon Wastewater, Acrylonitrile Wastewater, Fatty Acid Waste, Metal Chelate Solution, Sodium Cyanide Waste, Polyol Wastewater, Vitamin Fermentation Broth, Paint Booth Wash, Methyl Ethyl Ketone, Propylene Glycol, Carbon Tetrachloride, many other chemical compounds</td>
</tr>
</tbody>
</table>
Process Details

• HTP uses only pressurized hot water--no solvents
• Wet feedstock is made into water slurry with 15% to 35% dry equivalent solids
• Process is NOT supercritical, which is important to the overall economics and success of HTP
• Continuous process converts more than 99% of the feedstock organic content in 30-45 minutes
• Process is efficient--uses 15% of energy (85% free) when system is designed with heat integration
• Material of construction is Stainless Steel 316L
The Specific Case for Wood

• How does wood compare to other feedstocks?
• Algae may be the easiest of all biomass to process—converts efficiently and is generally easy to process
  – But there are no large algae farms
  – Algae is still far too expensive to use for fuels
• Wood is harder to process but still converts well
  – The difficulty is getting the wood into slurry form
  – When heated in water and pressure it liquefies quickly
Setup for Wood

- Wood generally produces acidic conditions
- Acid is corrosive to the stainless steel used in system
  - Acid also produces unwanted molecular forms and promotes polymerization of products
  - pH may be raised by addition of small amount of alkali to the wood slurry, preferably no lower than 6.0
- Size of wood particles depends on size of system
  - Size of particle no more than 25% of piping ID to prevent bridging--Bigger pipes mean less size reduction
  - So we want to get to bigger systems for wood
Combined Oil-Gas Hydrothermal Process Flow

1. Input Feed
   - Prepare Slurry
   - Pressurize & Heatup
   - HTL
   - Separate Oil & Water
   - Effluent Water
   - CHG
   - Separate Gas/Water

2. Bio-Oil
   - Upgrade & Refine
   - Gas
   - Water with Plant Nutrients

Genifuel
Products

• Bio-crude can be upgraded to refined fuels in a conventional refinery
  – May need pre-treater depending on refinery
• Methane can be used several ways
  – Use as fuel for generator to make electricity and heat
  – Remove CO$_2$, then inject into natural gas pipeline or use locally as CNG
  – Gas is clean (no sulfur, phosphorus, siloxanes)
• Most feedstocks produce fuels and power which are eligible for renewable incentives internationally
Products are Crude Oil, Methane Gas, or Both

Step 1 (HTL)
- HTL Bio-oil
- HTL Effluent Water

Step 2 (CHG)
- Upgraded Oil
- Step 2 (CHG)
- HTL Effluent Water

HYDROTREAT
- Clean Fuels
  - Jet
  - Diesel
  - Heavy

FRACTIONATE
- Clean Effluent Water
- Renewable Natural Gas

Products are Crude Oil, Methane Gas, or Both
- Type of feedstock has an effect on the properties of the liquids produced.
- The type of liquefaction processing also has an effect.
Water

- HTL process converts 35 to 50% of the biomass to oil; remaining biomass is in the HTL effluent water.
- Effluent water from the HTL process will have COD in range of 50,000 to 100,000.
  - Appearance is brownish water without visible solids.
- This water can be further processed with CHG to extract remaining energy and clean the water.
- After CHG water is sterile and clear with COD in range of 200 to 400; usually meets discharge standards.
Water (cont.)

- Water will contain all plant nutrients in original biomass except phosphorus,
- Phosphorus is recovered earlier in the process as a wet solid which can be processed into fertilizer in the same way as phosphate ore
- Nitrogen will be in the form of ammonia
- Following chart shows water analysis from a high-potassium algae species
## Analysis for CHG Effluent Water

<table>
<thead>
<tr>
<th>Element</th>
<th>Algae 4 composite water sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>K 766.490</td>
<td>7.186</td>
</tr>
<tr>
<td>Na 589.592</td>
<td>364.2</td>
</tr>
<tr>
<td>B 249.772</td>
<td>13.75</td>
</tr>
<tr>
<td>Si 251.611</td>
<td>11.03</td>
</tr>
<tr>
<td>Al 396.153</td>
<td>5.561</td>
</tr>
<tr>
<td>S 180.669</td>
<td>1.534</td>
</tr>
<tr>
<td>Ca 317.933</td>
<td>0.505</td>
</tr>
<tr>
<td>Ba 233.527</td>
<td>0.087</td>
</tr>
<tr>
<td>Cu 327.393</td>
<td>0.066</td>
</tr>
<tr>
<td>Sn 189.927</td>
<td>0.052</td>
</tr>
<tr>
<td>P 213.617</td>
<td>0.041</td>
</tr>
<tr>
<td>Mg 285.213</td>
<td>0.041</td>
</tr>
<tr>
<td>Fe 238.204</td>
<td>0.018</td>
</tr>
<tr>
<td>Mo 202.031</td>
<td>0.014</td>
</tr>
<tr>
<td>Zn 206.200</td>
<td>0.014</td>
</tr>
<tr>
<td>Ni 231.604</td>
<td>0.018</td>
</tr>
<tr>
<td>V 310.230</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn 257.610</td>
<td>0.005</td>
</tr>
<tr>
<td>Ti 334.940</td>
<td>0.002</td>
</tr>
<tr>
<td>Cr 267.716</td>
<td>0.002</td>
</tr>
<tr>
<td>Pb 220.353</td>
<td>0.002</td>
</tr>
</tbody>
</table>

*green is below quantifiable level of 1*
Status: Pilot System in Final Tests
Description of the Pilot System

- Pilot System capacity of 1 metric ton per day of wet algae slurry at 30% solids
- Will produce 1 barrel of oil per day
- Owner is a large oil refiner, who wants to test the system in a refinery environment
  - System is heavily instrumented and designed like a refinery system, with remote operating capability
  - Formal HAZOP review like a refinery system—but it is not a hydrocarbon system, it is a water system
  - Cost is USD $2.3 million
- A more typical system would be simpler and cheaper
Other Biomass to Fuel Technologies

• **Anaerobic Digestion (AD) is most widely known**
  – Biological process, more than 2,000 years old
  – Slow and incomplete conversion—app. 45% in 20 days vs. 99% in 45 minutes for hydrothermal

• **Cellulosic ethanol production**
  – 35% of carbon goes to fuel, vs. 85% for hydrothermal
  – Alcohol lower value than hydrocarbon fuels

• **Another technology—high-temperature pyrolysis—is not practical for wet materials**
  – 40% of the energy is lost drying the material
  – Output oil is lower energy and higher cost to refine
CHG Conversion Process

- The feedstock can either be raw biomass or the residual after formation and removal of HTL oil
- CHG uses a catalyst to convert liquefied biomass to methane (HTL uses no catalyst)
  - Catalyst is commercially available and produced in large quantities
  - Catalyst is pelletized in fixed bed in reactor pipes
- Sulfur and phosphate removal is accomplished in liquid state in several steps before the catalyst bed
- CHG of raw biomass achieves carbon conversion from wood to methane = 65%
CHG (Gas) Chemistry

Partial equations:

\[ C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2 \]  \hspace{1cm} \text{(steam reforming of carbohydrate)}

\[ CO + 3H_2 \rightarrow CH_4 + H_2O \]  \hspace{1cm} \text{(methanation)}

\[ CO + H_2O \rightarrow CO_2 + H_2 \]  \hspace{1cm} \text{(water-gas shift)}

The overall stoichiometry is then:

\[ C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3CO_2 \]

Notes:
1. Starch is used as an example, but actual feedstocks will contain many molecular structures.
2. The gas product will usually contain a small amount (1-2%) of hydrogen and ethane in addition to methane and carbon dioxide.
3. In practice, the gas will be approximately 60% CH\(_4\)/40% CO\(_2\), not 50/50 as shown because of feedstock differences.
Examples
# System Data 10 t/d Dry Weight Wood

<table>
<thead>
<tr>
<th>MEASURE</th>
<th>US UNITS</th>
<th>SI UNITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood dry weight/day</td>
<td>11.0 tons per day</td>
<td>10 t/d</td>
</tr>
<tr>
<td>Wood dry weight/year</td>
<td>3,857 tons per year</td>
<td>3,500 t/y</td>
</tr>
<tr>
<td>Slurry wet weight</td>
<td>55.1 tons per day</td>
<td>50 t/d</td>
</tr>
<tr>
<td>Gas with 60% methane</td>
<td>254 MCF per day</td>
<td>7,200 m³/d</td>
</tr>
<tr>
<td>Size of generator</td>
<td>875 kWe</td>
<td>875 kWe</td>
</tr>
<tr>
<td>Prime Mover Efficiency</td>
<td>NG IC Engine 40%</td>
<td>NG IC Engine 40%</td>
</tr>
<tr>
<td>Cost inc. genset</td>
<td>USD $12.8 million</td>
<td>CAD $14.4 million</td>
</tr>
<tr>
<td>Years to recover invest</td>
<td>28 Years</td>
<td>28 Years</td>
</tr>
</tbody>
</table>
# System Data for 30 MWe System

<table>
<thead>
<tr>
<th>MEASURE</th>
<th>US UNITS</th>
<th>SI UNITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood dry weight/day</td>
<td>303 tons per day</td>
<td>275 t/d</td>
</tr>
<tr>
<td>Wood dry weight/year</td>
<td>106,067 tons per yr</td>
<td>96,250 t/y</td>
</tr>
<tr>
<td>Slurry wet weight</td>
<td>1,516 tons per day</td>
<td>1,375 t/d</td>
</tr>
<tr>
<td>Gas with 60% methane</td>
<td>6,989 MCF per day</td>
<td>198,000 m³/d</td>
</tr>
<tr>
<td>Size of generator</td>
<td>30 MWe</td>
<td>30 MWe</td>
</tr>
<tr>
<td>Prime Mover Efficiency</td>
<td>CC Gas Turb 50%</td>
<td>CC Gas Turb 50%</td>
</tr>
<tr>
<td>Cost inc. genset</td>
<td>USD $109 million</td>
<td>CAD $122 million</td>
</tr>
<tr>
<td>Years to recover invest</td>
<td>4.2 years</td>
<td>4.2 years</td>
</tr>
</tbody>
</table>
Contact

James Oyler
President
Genifuel Corporation
801-467-9976 (Office)
jim@genifuel.com
www.genifuel.com

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