Liquefaction Technologies for Producing Biocrude for Jet, Diesel and Gasoline

JOHN HOLLADAY

Energy and Environment Directorate
Northwest Wood-Based Biofuels + Co-Products Conference, April 29, 2014
PNNL bioenergy research

Direct Liquefaction of Biomass
Producing catalysts and processes to make fuels directly from whole biomass (wet or dry)

Conversion of sugars and lignin
Producing new processes that make building blocks that are converted to chemicals and fuels

Refinery Integration
Developing solutions for co-processing biomass with fossil resources in existing infrastructure

Deliver Science & Technology to ensure sustainable incorporation of renewables into the fuel and chemical infrastructure

Catalysis
Applying fundamental and applied approaches to produce stable, active and selective catalysts able to operate in high water environments

Fungal Biotechnology
Improving microbes for producing fuel and chemical precursors from complex sugars - integrating processes with catalysis

Advanced Analysis
Addressing site-specific constraints through high resolution geographical info-physical models, processes economic and life cycle analysis
Catalyst R&D at PNNL at different scales

~1.4 ml 8-reactor packed bed system

40 ml dual T zone packed bed reactor

400 ml dual T zone packed bed reactors

1 L ebullated bed reactor

24 L 8-zone furnace packed bed reactor
Pyrolysis central challenge: Catalysis

Potential for distributed bio-oil production with processing in central facility

Pyrolysis and Liquefaction
- Are multiple variants
- Yield depends on quality of biomass feedstock and variant of technology
- Primary need for all variants is improved catalysis

Produce hydrocarbon fuels from low quality bio-oil, but...
- Catalyst life is too short
- Catalyst rate is too slow
Fuel characteristics

Desired Characteristics

- Miscible with petroleum-based fuels and transportable in current pipelines
- Meet performance & storability criteria designed for jet engines—it must be jet fuel
Pyrolysis enables 100% renewable jet

The hydroplane ran on 98% Bio-SPK and 2% renewable aromatics

<table>
<thead>
<tr>
<th></th>
<th>Jet A1 Spec</th>
<th>Starting SPK</th>
<th>Woody Pyrolysis Oil Aromatics-SPK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freeze Point (°C)</td>
<td>-47</td>
<td>-63</td>
<td>-53</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>39</td>
<td>42</td>
<td>52</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>0.775</td>
<td>0.753</td>
<td>0.863</td>
</tr>
</tbody>
</table>
Compound classes in jet fuels

**Ideal Carbon Length C8-C16**

<table>
<thead>
<tr>
<th>Compound Class</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>70 - 85%</td>
</tr>
</tbody>
</table>
| Normal Paraffins | H₃C⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻←  

We desire fuels with composition similar to above (i.e. a replacement or “drop-in” fuel)
Fast Pyrolysis and upgrading to fuels economics – 2009 estimate

Design Case Originally developed in 2009

- Process appears viable
- Research needs identified
- Catalyst maintenance appeared to have biggest impact initially
- Set research targets for out years
Fast pyrolysis and upgrading to fuels economics – 2009

Conversion costs – Integration of experimental results with modeled costs

- Reduced the catalyst replacement rate
- Costs to be completely updated Fall 2013
- Modest yield increase

Costs Projection:
- 2009 SOT: $7.19/gge
- 2010 SOT: $5.52/gge
- 2011 SOT: $4.51/gge
- 2012 SOT: $3.95/gge
- 2013 Projection: $3.18/gge
- 2014 Projection: $2.70/gge
- 2015 Projection: $2.54/gge
- 2016 Projection: $2.04/gge
- 2017 Projection: $1.73/gge
## Sensitivity Analysis - $/gallon change from base case

<table>
<thead>
<tr>
<th>Factor</th>
<th>Base Case</th>
<th>Base Case +40%</th>
<th>Base Case -40%</th>
<th>Base Case +25%</th>
<th>Base Case -25%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant Size, metric tons/day (4000 : 2000 : 1000)</td>
<td></td>
<td></td>
<td>-14.9%</td>
<td>17.8%</td>
<td></td>
</tr>
<tr>
<td>Internal Rate of Return, IRR (5% : 10% : 15%)</td>
<td></td>
<td></td>
<td>-14.5%</td>
<td>14.6%</td>
<td></td>
</tr>
<tr>
<td>Feedstock Cost, $/dry ton (60 : 80 : 120)</td>
<td></td>
<td></td>
<td>-6.9%</td>
<td>13.7%</td>
<td></td>
</tr>
<tr>
<td>Pyrolyzer Installed Cost (-40% : base : +40%)</td>
<td></td>
<td></td>
<td>-8.8%</td>
<td>8.8%</td>
<td></td>
</tr>
<tr>
<td>Hydrotreating Catalyst Life, yrs (2 : 1 : 0.5)</td>
<td></td>
<td></td>
<td>-6.8%</td>
<td>9.3%</td>
<td></td>
</tr>
<tr>
<td>FP yield + HT yield (64% FP+46% HT : 62%FP+44% HT : 60% FP+42% HT)</td>
<td></td>
<td></td>
<td>-8.5%</td>
<td>6.0%</td>
<td></td>
</tr>
<tr>
<td>Pyrolysis System, tpd (1x2000 : 2x1000 : 5x400)</td>
<td></td>
<td></td>
<td>-4.1%</td>
<td>7.0%</td>
<td></td>
</tr>
<tr>
<td>Hydrotreating yield, lb/lb pyrolysis oil (dry basis) (46%:44%:42%)</td>
<td></td>
<td></td>
<td>-5.3%</td>
<td>4.0%</td>
<td></td>
</tr>
<tr>
<td>Total Project Investment (-10% : base : +40%)</td>
<td></td>
<td></td>
<td>-1.2%</td>
<td>5.0%</td>
<td></td>
</tr>
<tr>
<td>HDO Reactors Capital (-40% : base : +40%)</td>
<td></td>
<td></td>
<td>-4.0%</td>
<td>4.1%</td>
<td></td>
</tr>
<tr>
<td>Stabilizer &amp; 1st HDO Stage Catalyst $/lb (30 : 60 : 90)</td>
<td></td>
<td></td>
<td>-3.2%</td>
<td>3.2%</td>
<td></td>
</tr>
<tr>
<td>Project Contingency (0% : 10% : 20%)</td>
<td></td>
<td></td>
<td>-3.3%</td>
<td>3.3%</td>
<td></td>
</tr>
<tr>
<td>2nd Stage HDO Reactor LHSV (0.4 : 0.22 : 0.1)</td>
<td></td>
<td></td>
<td>-1.3%</td>
<td>3.6%</td>
<td></td>
</tr>
<tr>
<td>Fast Pyrolysis yield, lb/lb wood (dry basis) (64% : 62% : 60%)</td>
<td></td>
<td></td>
<td>-3.5%</td>
<td>2.2%</td>
<td></td>
</tr>
<tr>
<td>1st and 2nd Stage HDO @ 1200 psia</td>
<td></td>
<td></td>
<td>-4.4%</td>
<td>-0.5%</td>
<td>-0.6%</td>
</tr>
<tr>
<td>1st and 2nd Stage HDO @ 1600 psia</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen Plant Installed Cost (-25% : base : +25%)</td>
<td></td>
<td></td>
<td>-1.9%</td>
<td>2.4%</td>
<td></td>
</tr>
<tr>
<td>Stabilizer Reactor LHSV (1 : 0.5 : 0.3)</td>
<td></td>
<td></td>
<td>-2.4%</td>
<td>2.4%</td>
<td></td>
</tr>
<tr>
<td>2nd HDO Stage Catalyst $/lb (10 : 15.5 : 30)</td>
<td></td>
<td></td>
<td>-1.6%</td>
<td>2.1%</td>
<td></td>
</tr>
<tr>
<td>Hydrocracker Size (None : base : 2x)</td>
<td></td>
<td></td>
<td>-1.0%</td>
<td>2.8%</td>
<td></td>
</tr>
<tr>
<td>Compressor Capital (-40% : base : 40%)</td>
<td></td>
<td></td>
<td>-2.0%</td>
<td>1.2%</td>
<td></td>
</tr>
</tbody>
</table>
Deactivation of $\text{RuS}_x/C$ leads to unstable material, which forms “char” resulting in reactor plugging in < 100 h

$\text{CoMoS}_x/C$ also exhibits limitations to its catalyst life and deactivation occurs over <100 h campaign

Elliott et al Energy Fuels 2012, 26, 3869
Previous long-term catalytic experiments (ca. 2011) reached only ~ 100 hour without plugging.

- FP oil density: 1.2 g/cc
- Catalysts: RuS/C, CoMoS/C
- T: 250 - 410°C
- P: 15 MPa H₂
- Space velocity: 0.1-0.2

Start-up after each plugging event required replacement of about 10% of the catalyst bed.
State of the art: No plugging after 60 days on stream

- 2013 milestone on extended lifetime testing was completed successfully
- Higher yield and lower oxygen content at higher temperatures were achieved
- Long-term catalyst deactivation still present as indicated by increased density

Slide courtesy of A. Zacher
Sustainability pyrolysis oil with upgrading

Life cycle GHGs for gasoline from fast pyrolysis and upgrading

- 2017 goal case assumes better yields and economics, but has slightly higher GHGs
- Higher yields lower feedstock contribution but increase conversion contribution
- Preliminary indications are that fuel derived from fast pyrolysis of wood and bio-oil upgrading appears to be >60% GHG reduction (cellulosic biofuel), however, qualification under the RFS is determined by the EPA
What is next: *Ex situ* catalytic fast pyrolysis (vapor upgrading)

Catalyst Summary
- **Generation 1**: PNNL modified zeolite, spent FCC catalysts blend (low-cost)
- **Generation 2**: Stable, strong, multifunctional, catalysts designed for *in situ* HDO

**BIOMASS**
- Upgrade small oxygenates to fuel range compounds
- Generate H₂ from CO and small oxygenates for *in situ* HDO

**Ex situ Catalytic Fast Pyrolysis**
- Fast Pyrolysis
- Ketonization Condensation
- Water Gas Shift Reforming HDO

**Hydrotreatment**
- Less gas formation
- Less H₂ consumption
- Decrease O/C
- Improve stability
- Optimize composition

**Intermediate BIO-OIL**

**Fuels**

**Improved Carbon and Hydrogen efficiency**

Catalyst Summary
- ✓ Generation 1: PNNL modified zeolite, spent FCC catalysts blend (low-cost)
- ✓ Generation 2: Stable, strong, multifunctional, catalysts designed for bio-oil
Co-processing bio-oil with petroleum FCC oils (vacuum gas-oils)

- Understand minimum upgrading of bio-oil for co-processing
- Develop FCC catalysts tuned for bio-oil VGO mixtures
- Understand quality of product
- Determine fate of biogenic carbon in the process

Tesoro Refinery, Anacortes, WA (Scott Butner, PNNL)
Hydrothermal liquefaction for improved oil

Hydrothermal Liquefaction
- Feed: whole biomass + buffer (10 to 20 wt% solids)
- Operation: condensed phase
- Bio-oil: gravity separable; (oxygen: 10 to 20 wt%)
- Product yield: ~50%-carbon; 32%-mass

Bio-oil Upgrading
- Operation: feed is thermally stable, low H₂ required
- Yield: 94%-carbon; 84%-mass; 95%-volume
- Product: high yield to distillate range
# Liquefaction of Biomass to Bio-Oils

## Conditions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Fast pyrolysis</th>
<th>Hydrothermal liquefaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>feedstock</td>
<td>Dry Biomass</td>
<td>Wet biomass</td>
</tr>
<tr>
<td>operating temperature</td>
<td>450-500°C</td>
<td>350°C</td>
</tr>
<tr>
<td>environment</td>
<td>inert gas</td>
<td>aqueous condense phase</td>
</tr>
<tr>
<td>catalyst</td>
<td>none</td>
<td>alkali reagent often used</td>
</tr>
<tr>
<td>operating pressure</td>
<td>1 atm</td>
<td>200 atm</td>
</tr>
<tr>
<td>residence time</td>
<td>&lt; 1 sec</td>
<td>5 to 30 min</td>
</tr>
<tr>
<td>carbon yield to bio-oil</td>
<td>70% (~40% to HC)</td>
<td>50% (typical for lignocellulosics)</td>
</tr>
</tbody>
</table>

## Oil Product Quality

<table>
<thead>
<tr>
<th></th>
<th>Fast pyrolysis</th>
<th>Hydrothermal liquefaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>heating value (HHV)</td>
<td>6,900 Btu/lb</td>
<td>14,200 Btu/lb</td>
</tr>
<tr>
<td>oxygen content</td>
<td>40%</td>
<td>15%</td>
</tr>
<tr>
<td>water content</td>
<td>25%</td>
<td>5%</td>
</tr>
<tr>
<td>viscosity@40°C</td>
<td>low (50 cSt)</td>
<td>high (4,000 cSt)</td>
</tr>
<tr>
<td>thermal stability</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

*cSt = centistokes*
PNNL HTL hybrid reactor (plug flow)

Small CSTR at critical temperature transition
HTL bio-oil quality

Stage 2 Carbon Yields in Hybrid System

- 130 h on-stream, 7 L bio-oil
- Mean balance: Wood 99% (Mass) and 88% (carbon)
- Mean balance: Corn stover 96% (Mass) and 83% (carbon)
- Lower yield to bio-oil from corn stover observed

<table>
<thead>
<tr>
<th></th>
<th>Pine</th>
<th>Corn Stover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen (Dry)</td>
<td>12%</td>
<td>17%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.29%</td>
<td>1.1%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.01%</td>
<td>0.04%</td>
</tr>
<tr>
<td>Moisture</td>
<td>9%</td>
<td>8%</td>
</tr>
<tr>
<td>Density, g/ml</td>
<td>1.11</td>
<td>1.10</td>
</tr>
<tr>
<td>Viscosity, cSt, 40°C</td>
<td>3100</td>
<td>3400</td>
</tr>
<tr>
<td>Oil TAN mgKOH/g</td>
<td>55</td>
<td>44</td>
</tr>
</tbody>
</table>

[Graph showing carbon yields for Pine and Corn Stover in Bio-oil, Aqueous, Gas, and Solids]
Simulated distillation data (fuel quality)

Product composition
- 7% paraffin
- 47% cycloparaffin
- 46% aromatic

Shift the product to the distillate range
Carbon efficiency achieved

<table>
<thead>
<tr>
<th>Step</th>
<th>Carbon Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTL</td>
<td>62%</td>
</tr>
<tr>
<td>Hydrotreat</td>
<td>96%</td>
</tr>
<tr>
<td>Combined</td>
<td>60%</td>
</tr>
</tbody>
</table>
Technoeconomic considerations

Applied Energy (2014) Yunhua Zhu¹,*, Mary J. Biddy², Susanne B. Jones¹, Douglas C. Elliott¹, Andrew J. Schmidt¹

Feed
• 2000 MT/day

Yield
• (SOT) 44 M GGE/y
• (goal) 70 M GGE/y

Energy Efficiency
• (SOT) 52%
• (goal) 66%

<table>
<thead>
<tr>
<th>Feed</th>
<th>SOT</th>
<th>Goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>44 M GGE/y</td>
<td>70 M GGE/y</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>52%</td>
<td>66%</td>
</tr>
</tbody>
</table>

Average return on investment
45.4

MFSP, $/L product
1.29

MFSP, $/GGE product
4.44

MFSP, $/GGE product
0.74

2.52
HTL life cycle analysis

- No co-products; allocation and displacement results are the same
- HTL emits 83% less GHG vs. diesel or gasoline
- Sensitivity: 50% increase in yield increases GHG reduction by ~5%

WTW GHG emissions comparison

Sensitivity analysis results
Hydrothermal Liquefaction - Feedstocks

- Algae Paste
- Algae HTL Oil
- Hydrotreated Algae HTL Oil
- Wood Paste
- Wood HTL Oil
- Hydrotreated Wood HTL Oil
Upgraded HTL oil from algae: 85% diesel (paraffinic)
Alcohol to Jet Fuel (ATJ) Collaborative

A novel route to Drop-in hydrocarbon Fuels with a low cost, low value feedstock

LanzaTech Technology

Gas Feed Stream

Gas Reception

Fermentation

Recovery

Alcohol Product

Catalytic Conversion

Separation

Diesel

Jet

Gasoline

IAF/PNNL Technology
Fuel test results from 2012

- PNNL prepared samples for fuel property evaluation
- Off-site specification testing conducted by AFRL
- Positive results with continued focus on improving yields and limiting aromatics

<table>
<thead>
<tr>
<th>Specification Test</th>
<th>MIL-DTL-83133H Spec Requirement</th>
<th>PNNL-1</th>
<th>PNNL-2</th>
<th>FT-SPK</th>
<th>JP-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics, vol %</td>
<td>≤25</td>
<td>1.9</td>
<td>2.2</td>
<td>0.0</td>
<td>18.8</td>
</tr>
<tr>
<td>Olefins, vol %</td>
<td></td>
<td>1.2</td>
<td>1.1</td>
<td>0.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Heat of Combustion (measured), MJ/Kg</td>
<td>≥42.8</td>
<td>43.1</td>
<td>43.1</td>
<td>44.3</td>
<td>43.3</td>
</tr>
<tr>
<td>Distillation:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP, °C</td>
<td></td>
<td>161</td>
<td>165</td>
<td>144</td>
<td>159</td>
</tr>
<tr>
<td>10% recovered, °C</td>
<td>≤205</td>
<td>165</td>
<td>171</td>
<td>167</td>
<td>182</td>
</tr>
<tr>
<td>20% recovered, °C</td>
<td></td>
<td>166</td>
<td>173</td>
<td>177</td>
<td>189</td>
</tr>
<tr>
<td>50% recovered, °C</td>
<td></td>
<td>171</td>
<td>183</td>
<td>206</td>
<td>208</td>
</tr>
<tr>
<td>90% recovered, °C</td>
<td></td>
<td>190</td>
<td>220</td>
<td>256</td>
<td>244</td>
</tr>
<tr>
<td>EP, °C</td>
<td>≤300</td>
<td>214</td>
<td>243</td>
<td>275</td>
<td>265</td>
</tr>
<tr>
<td>T90-T10, °C</td>
<td>22</td>
<td>25</td>
<td>49</td>
<td>89</td>
<td>62</td>
</tr>
<tr>
<td>Residue, % vol</td>
<td>≤1.5</td>
<td>1.1</td>
<td>1.1</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Loss, % vol</td>
<td>≤1.5</td>
<td>1</td>
<td>0.8</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>≥38</td>
<td>44</td>
<td>48</td>
<td>45</td>
<td>51</td>
</tr>
<tr>
<td>Freeze Point, °C</td>
<td>≤-47</td>
<td>&lt;=-60</td>
<td>&lt;=-60</td>
<td>-51</td>
<td>-50</td>
</tr>
<tr>
<td>Density @ 15°C, kg/L</td>
<td>0.775 - 0.840 (0.751 - 0.770)</td>
<td>0.803</td>
<td>0.814</td>
<td>0.756</td>
<td>0.804</td>
</tr>
</tbody>
</table>
LanzaTech is key partner - Recycling carbon for production of alcohol

Source: LanzaTech
Next steps

- Securing tolling facility for production of renewable jet fuel currently for larger volume demands in 2014
- Ethanol will be supplied from Lanzatech’s facilities in China or India
- Technology used for tolling will be supplied by PNNL/IAF
- Fuel production would occur in 2014 with test flights to follow
  - Will include enough production to facilitate ASTM certification process
- Anticipating additional scale up in 2016
Producing fuels from whole biomass: Liquefaction technology

PNNL applying it’s core capability in catalysis to solve the unique challenges of producing hydrocarbons from direct liquefaction.

Impact:
Research is advancing biofuels to serve refinery industry needs
- Demonstrated fuel quality (UOP)
- Developed Process models and design case
- Solved initial catalyst life issue
- Developed improved process
- Partnering with industry to co-process bio-oil with petroleum

PNNL is developing new, robust catalyst to make higher quality, stable, bio-oils and refining technologies to convert bio-oils to fuels.

PNNL provides unique suite of continuous reactor capacity and is partners with industry and others in deploying new technologies.

Core Capabilities

<table>
<thead>
<tr>
<th>Catalysis</th>
<th>Computational modeling</th>
<th>Continuous reactor capability</th>
<th>Process and Life-cycle Analysis</th>
</tr>
</thead>
</table>

Funding source: DOE Office of Energy Efficiency and Renewable Energy
Success Story: Aviation Biofuels

PNNL is working to improve and expand the use of cost-effective, bio-based aviation fuels

Impact:
Research is advancing biofuels to serve aviation industry needs

- PNNL delivers aviation biofuels in 2012 to Air Force for testing
- PNNL and partners produce first 100% biomass-derived jet fuel, used in hydroplane
- PNNL co-leads key DOE biofuels research consortiums

Core Capabilities

| Catalysis | Biotechnology | Fuel Chemistry | Process and Life-cycle Analysis |

Funding source: DOE Office of Energy Efficiency and Renewable Energy
Conclusions

- The last 2 years has resulted in tremendous strides that address critical issues in liquefaction.
- Liquefaction technologies will lead to cyclic hydrocarbons (unless ring opening catalysts are employed).
- Hydrogen demand varies by technology.
- Alcohol to jet moves us out of the classical liquefaction paradigm.

The hydroplane ran on 98% Bio-SPK and 2% renewable aromatics.
Thank you for your time

- Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy (Bioenergy Technologies Office)

- Special thanks to Alan Zacher, Andy Schmidt, Huamin Wang, Mariefel Olarte, Sue Jones, Doug Elliott and many great researchers who carried out the work
Other Feedstock Resources – Better Utilize Wastes

- Roosevelt Landfill
  - 81 percent of permitted disposal in WA
  - 3 unit trains arrive daily (100 unit cars each)

- Columbia Ridge Landfill
  - 85% of permitted waste in OR
  - 2009 waste from CA and HI
  - 14 million tons of material waste produced
    - Recycling diverts 6 million (some of this is composted)

- 7-8 million tons of organic available (all at less than $50 per ton)

Waste could be a primary feedstock
- Municipal solid waste, wet wastes, gas wastes
- How to improve RINs