Refinery Integration of Renewable Feedstocks

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CAAFI R&D SOAP-Jet webinar series
November 14, 2014
Overview

► Fuel characteristics
► Refinery overview
► Modeling assessments
  ■ National Advanced Biofuels Consortium (NABC)
  ■ Opportunities
► Technology advancements
  ■ FCC (co-processing VGO with bio-oil)
  ■ Hydrotreating (bio-oil and biocrude)
  ■ Alkylation (alcohol to jet)
► Conclusions and next steps
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
- Optimize desired hydrocarbon chain/boiling point for aviation (mid-distillates)

Lower cost
- Reduce H₂ demand and pressure
- Improve product quality
Iso-paraffins and n-paraffins are good (Btu content)

Aromatics are bad above certain amount (minimum needed to ensure seal swell)

Fractions vary!

Jet is designed around propulsion system
Hydrocarbon mixture gives properties needed
- Energy density
- Freeze point
- Flash point
- Lubricity
- etc

Source: Dr. Timothy Edwards, Air Force Research Laboratory
Aromatics in jet fuel also helps elastomers in the fuel system to swell and seal properly at low temperature.

Iso-paraffins and n-paraffins are good (Btu content) / Aromatics are bad above certain amount (minimum needed to ensure seal swell).
Refineries

- Capital cost
- Unit operations within the refinery
- Insertion points

Tesoro Refinery, Anacortes, WA (Scott Butner, PNNL)
**Capital costs – Plant size and economies of scale**

<table>
<thead>
<tr>
<th>Cellulosic Biorefinery</th>
<th>Corn Ethanol</th>
<th>Fischer-Tropsch (CTL)</th>
<th>US Petroleum Refinery</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;5,000 bpd</td>
<td>5,000 - 10,000 bpd</td>
<td>US – 8,000 bpd</td>
<td>up to 550,000 bpd</td>
</tr>
<tr>
<td></td>
<td></td>
<td>China – 30,000+ bpd</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>South Africa – 160,000 bpd</td>
<td></td>
</tr>
</tbody>
</table>

- **US Petroleum Refinery**
  - up to 550,000 bpd

**Bpd = barrels per day liquid fuels**

- **Cellulosic Biorefinery**
  - <5,000 bpd

- **Corn Ethanol**
  - 5,000 - 10,000 bpd

- **Fischer-Tropsch (CTL)**
  - US – 8,000 bpd
  - China – 30,000+ bpd
  - South Africa – 160,000 bpd

- **US Petroleum Refinery**
  - up to 550,000 bpd

**Costs**

- **Cellulosic Biorefinery**
  - $77,000 — 285,000/bpd (US DOE)

- **Corn Ethanol**
  - $16,000 — 34,000/bpd (USDA)

- **Fischer-Tropsch (CTL)**
  - Biomass to liquid, 5,000 bpd (Fischer-Tropsch):
    - $68,000 — 408,000/bpd (Robert Malina)

- **Refinery conversions**
  - $0 — 140,000/bpd (CERA)

**Sources**

- [USDA](http://www.usda.gov/oce/reports/energy/EthanolSugarFeasibilityReport3.pdf)
- [CERA](http://www.ihs.com/pdfs/ihs-cera-upgrading-refining-mar-2013.pdf)

* Sassol proposed GTL facility in Louisiana
  - 96,000 bpd facility est. cost $145,000/bpd
**Bioprocessing and today’s infrastructure**

Refining

- Complex but efficient
- ~100 years experience
- ~750 refineries
- ~85M BBL of crude refined daily
- ~50M BBL transport fuels; ~6M BBL of aviation fuel (~250 M gallons/day; 90 B gallons/year)

Scientific/technical Challenge

- Catalysts developed for the petrochemical and refining industries are generally not stable to bioprocessing
- Engineering (materials of construction, etc)
Renewables may be added to petroleum refineries at different locations.
- The easiest is as a blendstock (insertion point 3),
- Greater capital savings may occur if the renewables use refinery unit operations for processing (Insertion 2)
Crude units separate molecules do not chemically alter the material that they process.

Contaminants would be spread throughout the refinery rather than be concentrated into facilities that are best able to handle these materials.

Many refineries produce jet fuel directly from the crude unit.

 Insertion point 1 (blending renewable materials into crude) is not viable unless the material is essentially purely composed of carbon and hydrogen, with minimal levels of olefins.
Biomass is converted to a near-finished fuel or blendstock

- Blended component must meet all applicable standards (ASTM) for finished fuel

- Allows tailoring processes to unique properties of biomass

- Allows blending to be controlled by refiner

- Strict rules on blending outside of the refinery may require re-testing of controlled properties

- Allow use of infrastructure for moving fuels around
- The right renewable can provide value to a refinery (bringing low value refinery streams to spec)
Conversion processes
- Hydrocrackers
- Fluid catalytic crackers (FCC)
- Cokers

Finishing processes
- Hydrotreating
  - Naphtha HT
  - Distillate HT
  - etc
- Specialty units
  - Isomerizing
  - Reforming
  - Alkylating

- **Must not harm catalyst or reactor (carbon steel)**
- **Product yield cannot be reduced**
- **Product quality cannot be compromised**
Conversion Processes

- Decreases molecule sizes to convert heavier materials into distillation ranges of transportation fuels
- Conversion units are also capable of removing some level of contaminants

<table>
<thead>
<tr>
<th>Unit</th>
<th>C:H increase mode</th>
<th>Cracking mode</th>
<th>Feedstock</th>
<th>Feed boiling Range (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coker</td>
<td>C rejection as coke</td>
<td>Thermal</td>
<td>Vacuum resid</td>
<td>1050+</td>
</tr>
<tr>
<td>FCC</td>
<td>C rejection as coke</td>
<td>Fluid catalyst</td>
<td>Vacuum gas oil</td>
<td>610-1050</td>
</tr>
<tr>
<td>Hydro-cracker</td>
<td>H addition using metal cat</td>
<td>Fixed bed catalyst</td>
<td>Vacuum gas oil</td>
<td>450-1050</td>
</tr>
</tbody>
</table>

- Thermal processes affected by free radical generators/traps
- Acid catalysts affected by basic poisons (eg. alkali) & metals

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Hydrotreaters

- Remove heteroatoms (such as S, N, O) via catalytic reaction with H₂
  - Allow finished products to meet spec or to protect sensitive units
- Hydrotreating does not materially impact carbon chain length
  - Renewable feedstocks need to be introduced with a compatible chain length to allow on-spec production of fuels

<table>
<thead>
<tr>
<th>Service</th>
<th>Feed Boiling Range</th>
<th>Temperature</th>
<th>Pressure</th>
<th>LHSV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>90-380° F</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kerosene/Diesel</td>
<td>380-610° F</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum gas oil</td>
<td>610-1050° F</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Red arrows indicate desired direction to move

- Trickle bed reactors contain fixed bed of sulfided NiMo- or CoMo/Al₂O₃ catalyst particles
  - Sensitive to fouling via solids deposition, coking or polymerization Deactivation via metals, alkali, bio-heteroatoms (eg. P)
  - May have challenges with heat gain across “standard” refinery hydrotreaters may exceed allowable temperature limits
“Specialty” Units

- **Isomerizing**
  - Converts n-paraffins to isomers (higher octane or alkylation feed)
  - Fixed bed of metal/acid catalyst at lower temp than reforming

- **Alkylating**
  - Converts isobutane & isobutylene to isoctane
  - HF or H$_2$S acid catalyst (containment!!), sensitive to feed carbon number

- **Reforming**
  - Upgrades octane of naphthas by generation of aromatics (+ H$_2$) from napthenes (+ paraffins)
  - Fixed bed of chlorided Pt/Al$_2$O$_3$ catalyst particles at low pressure & high temp, sensitive to S, N in the feed
DOE’s Bioenergy Technologies Office sponsored analysis on refinery integration

Technical Focus
- High level assessment of impact of incorporation of bio-derived intermediates in U.S. petroleum refineries
- Surveys availability of biomass near petroleum refineries in the 2022 timeframe
- Preliminary considerations of bio-intermediate compatibility with petroleum intermediates
- Offers a refiner’s perspective
- Public document

Mission Impacts Supports understanding of infrastructure use
- Addresses entire barrel
- Considers advanced biofuels

Data Sources
- KDF for biomass resources
- EIA for refinery resources
- Publically available bio-intermediate data

High-level impact assessment

What refining capacities and capabilities currently exist in the US?

- Per EIA, 149 refineries total, 136 sufficiently detailed
- ~20 million barrels/day total capacity (136 refineries)
- Categorized into three main types:
  - Non-conversion & non-hydrotreating
  - Middle-distillate hydrotreating capability
  - Full conversion – fluidized catalytic cracking and hydrocracking
Survey of projected 2022 biomass availability near petroleum refineries

Q: Proximity of biomass suitable for 20% co-processing?

A: Initial look suggests refineries & biomass may fit

Refinery sites with highest likelihood of biofuel production**

* 20% additional yield loss
$60/ton farm gate
85 gal/dry ton conversion

**US refinery sites with highest est. fuel volumes
100 mile radius around each refinery
FCC and HCK refineries only (Cat 3)
Equiv. biofuel intermediate into any refinery limited to 20% of total crude capacity

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## Refiner’s perspective

### – safety, reliability, predictability, profitability –

<table>
<thead>
<tr>
<th>Risk</th>
<th>Type of Bio-oil Intermediate</th>
<th>Insertion</th>
<th>Refinery Challenges</th>
</tr>
</thead>
</table>
| Lowest    | Well defined, consistent quality, such as single molecules (e.g., ethanol, butanol, farnesene) | Blending units                             | - Blending, product performance and distribution of products that include the bio-component  
- Evaluating and managing potential stability, toxicity and environmental issues |
| Medium    | Intermediates requiring only minor treating (e.g. triglycerides, some direct liquefaction oils, some catalytically derived sugar oils) | Hydrotreating followed by blending         | Challenges identified above, plus:  
- Understanding process performance on new feeds and blends with petroleum-based feeds  
- Enabling larger fractions of bio-oil blending stocks while still meeting product specs.  
- Providing sufficient hydrogen to meet hydrotreating demands (for reducing oxygen or aromatic contents) |
| Highest   | Intermediates needing boiling range & composition changes for acceptable gasoline, diesel and jet fuel blending stocks (e.g. fast pyrolysis oils, some hydrothermal liquefaction oils, some catalytic pyrolysis oils) | Off-site or dedicated on-site hydrotreating followed by cat- or hydro-cracking | Challenges identified above, plus:  
- Understanding the impact of bio-oils on all refinery processes  
- Meeting product quantity and quality needs with feedstocks with less data on conversion behavior |
Preliminary Conclusions

- Focus on Gulf Coast
  - Biomass availability, river logistics
  - Primary supply is imported crude (priced off Brent)
  - Limited access to Bakken, Marcellus/Utica, Canadian supplies
- Need to improve bio-intermediate characterization
  - Develop metrics that are meaningful to refineries (pour point, cetane, API, D86, etc)
  - Improve predictions of how the biomaterials will process within the refinery
- Significant risk for co-processing that will need to be reduced
Technology development

- FCC
- Hydrotreating/hydrocracking
- Alkylation
Fluid catalytic cracking

Co-feed to the Fluid Catalytic Cracking (FCC) unit is a favored option

Give data on two bio-oil FCC feed options

Results – Vegetable oil feed
Results – Pyrolysis oil feed
Continuous circulating riser
Work done in WR Grace DCR™ pilot plant

26 licensed DCR pilot units have been constructed throughout the world

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## FCC yields of soybean oil vs vacuum gas oils

<table>
<thead>
<tr>
<th></th>
<th>100% Soybean Oil</th>
<th>100% VGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/O Ratio</td>
<td>6.7</td>
<td>9.3</td>
</tr>
<tr>
<td>H2 Yield wt%</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>C1 + C2's wt%</td>
<td>1.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Total C3 wt%</td>
<td>4.3</td>
<td>6.7</td>
</tr>
<tr>
<td>Total C4 wt%</td>
<td>6.2</td>
<td>12.4</td>
</tr>
<tr>
<td>Gasoline (C5-430°F) wt%</td>
<td>44.5</td>
<td>53.1</td>
</tr>
<tr>
<td>G-Con RON EST</td>
<td>90.9</td>
<td>90.2</td>
</tr>
<tr>
<td>G-Con MON EST</td>
<td>79.0</td>
<td>79.5</td>
</tr>
<tr>
<td>LCO (430-700°F) wt%</td>
<td>22.0</td>
<td>15.4</td>
</tr>
<tr>
<td>Bottoms (700°F+) wt%</td>
<td>3.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Coke wt%</td>
<td>4.6</td>
<td>5.2</td>
</tr>
<tr>
<td>Fuel Gas CO (wt%)</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Fuel Gas CO₂ (wt%)</td>
<td>0.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Fuel Gas H₂O (wt%)</td>
<td>10.3</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Compared to vacuum gas oil, soybean oil produces less gasoline and more light cycle oil (LCO).

### Conditions
- Rx exit temp = 970°F
- Catalyst temp = 1300°F
- Feed temp = 250°F
- Pressure = 25 psig

Vegetable oil is chemically as close to petroleum as any biomass feedstock.

Not favored technology for jet fuel from veg. oils.
Key findings – soybean oil

- Soybean oil cracking changes the riser temperature profile
  - Heat of cracking is only ~15% of conventional VGO
- Most of the oxygen reacts to form water
- Product yield slate is different
  - Sharply lower gasoline
  - Sharply higher Light cycle oil, lower bottoms

Soybean oil could likely be processed in a commercial FCC unit
Processing a blend of pyrolysis oil and VGO

- Co-processing bio-based pyrolysis oil with conventional vacuum gas oil (VGO)
- Processing pyrolysis oil isn't easy and requires changing (co)feed systems; adding surfactants and riser modifications

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content (wt%)</td>
<td>23.0</td>
</tr>
<tr>
<td>Carbon (as-is) (wt%)</td>
<td>39.5</td>
</tr>
<tr>
<td>Hydrogen (as-is) (wt%)</td>
<td>7.5</td>
</tr>
<tr>
<td>Oxygen (as-is) (wt%)</td>
<td>53.0</td>
</tr>
<tr>
<td>Carbon (dry basis) (wt%)</td>
<td>55.5</td>
</tr>
<tr>
<td>Hydrogen (dry basis) (wt%)</td>
<td>6.5</td>
</tr>
<tr>
<td>Oxygen (dry-basis) (wt%) (by difference)</td>
<td>38.0</td>
</tr>
</tbody>
</table>

Pyrolysis oil is a challenging feed!

This is what happened to the drive strap on a gear pump when it seized while pumping 100% pyrolysis oil
Yield when blending in 3 wt% pyrolysis oil

Even small amounts (3 wt%) of pyrolysis oil result in significant yield shifts

- A majority of the pyrolysis oil converts to H₂O, CO and CO₂
- Incremental yields of coke and bottoms are also very high
- Gasoline and LCO decrease

Economics will likely preclude co-processing raw pyrolysis oil in an FCC

Adding raw pyrolysis oil results in more coke, less gasoline and less LCO
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)
<table>
<thead>
<tr>
<th>Degree of Catalytic Hydrotreating (O content, dry basis)</th>
<th>Maximum VGO feed preheat temperature without nozzle plugging</th>
<th>Percentage pyrolysis oil co-processed</th>
<th>Yield Observations while coprocessing</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (38 wt% O)</td>
<td>~200°F (93°C)</td>
<td>up to 5 wt% with difficulty</td>
<td>Increased coke, reduced gasoline</td>
</tr>
<tr>
<td>Mild (22 wt% O)</td>
<td>~200°F (93°C)</td>
<td>up to 3 wt% with difficulty</td>
<td>Increased coke, reduced gasoline</td>
</tr>
<tr>
<td>Medium (11% O)</td>
<td>Up to 700°F (370°C)</td>
<td>10 wt%</td>
<td>Yields similar to VGO</td>
</tr>
<tr>
<td>Severe (2% O)</td>
<td>Up to 700°F (370°C)</td>
<td>10 wt%</td>
<td>Yields similar to VGO</td>
</tr>
</tbody>
</table>

Note: typical FCC feed pre heat temperatures are 300 to 700°F (150-370°C). Pyrolysis oil levels >10 wt% were not tested since refineries are unlikely to run above these levels.
Other advancements (FCC)

- Ensyn is working on refinery co-processing to produce gasoline and diesel
- Report it to be “in final stages of commercialization”
- 5% blend of RFO™ (pyrolysis oil) with VGO oils for production of spec gasoline and diesel
- Testing done in bench units, pilot units and commercial FCC units
- 2015 extended commercial demonstration
- “Eligible under EPA’s RFS2 program for the generation of D3 [co-processing] and/or D7 [heating oil] cellulosic RINs.”
PNNL’s Ongoing work

- Analysis of corrosion coupons included during co-processing runs
  - Corrosion can be partially addressed through bio-oil stabilization (e.g. light hydrotreating)
- Carbon accounting using isotope analysis
- Oxygen analysis of liquid products
- Full characterization from co-processing of straw based pyrolysis oils
Hydrotreating

Work done at PNNL

Current studies are on hydrotreating neat bio-oil

Fast pyrolysis bio-oil
- Bio-oil is not miscible with petroleum
- Severe catalyst challenges

Hydrothermal Liquefaction biocrude
- Moves further into mid-distillate/distillate range
- More miscible with petroleum
- Easier to process
Relative H₂ demands in the refinery

- Hydrotreating is designed primarily to remove S and N; removing the large amount of O in biomass may add additional H₂ demand to refineries.
- Slides that follow will examine pyrolysis bio-oil hydrodeoxygenation (HDO) and Hydrothermal liquefaction biocrude HDO.

H₂ chemical consumption, scf/bbl fd (standard cubic feet/barrel feed)

<table>
<thead>
<tr>
<th>Petroleum hydrodesulfurization</th>
<th>Petroleum hydrocracking</th>
<th>Pyrolysis oil</th>
<th>HTL biocrude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naptha HDS</td>
<td>Kerosene HDS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ATM resid HDS</td>
<td>Gas oil HDS</td>
<td>Mild HCK</td>
<td>HDO</td>
</tr>
<tr>
<td>45</td>
<td>555</td>
<td>460</td>
<td>~3400</td>
</tr>
<tr>
<td>422</td>
<td></td>
<td>358</td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td></td>
<td>660</td>
<td>~1800</td>
</tr>
<tr>
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</tr>
</tbody>
</table>
Hydrotreating reactor configurations and scales

Workhorse equipment

~1.4 cc 8-reactor packed bed system

40 cc dual T zone packed bed reactor

400/800 cc dual T zone packed bed

1 L ebullated bed reactor

19 L 8-zone furnace packed bed
Raw bio-oil leads to plugging (short as 20-50 h on stream)

- 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
- H₂ demand = 5 - 8 g H₂/100 g oil (dry basis)

Start-up after each plugging event required replacement of about 10% of the catalyst bed

Understanding of plug formation JACS 2014. DOI: 10.1021/ja501592y
Through mild pretreatment we can produce an oil that is processable.

A. Zacher

PNNL demonstrated a fourfold increase in stable on-stream production time, and a threefold increase in weight hourly space velocity (throughput).

Reduction in state-of-technology conversion cost of 60% from $12/gge in 2009 to $4.60/gge today (note: gge = gasoline gallon equivalent).
Vacuum distillation curves for hydroprocessed pyrolysis bio-oil (wood)

Jet fuel mid-distillate may provide the aromatic/cyclic portion of jet fuel
Future possibility of 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</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>
Pyrolysis oil summary

Jet A, JP-8

Products

- HDCJ (Kior)
- CH (UOP)

Feedstock

- Forest residues
- Agriculture residues

Pyrolytic methods make cyclics and aromatics

Source: Dr. Timothy Edwards, Air Force Research Laboratory
# Liquefaction of biomass (FP vs HTL)

<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 bar</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%</td>
<td>50% (typical for lignocellulosics)</td>
</tr>
<tr>
<td>oil product quality</td>
<td>Pyrolysis bio-oil</td>
<td>HTL Biocrude</td>
</tr>
<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
Hydrothermal liquefaction (HTL)

Reactor configuration: plug flow

Typical HTL operation at 350°C, 200 bar; Reactor: 200 to 2,000 mL
(note: at bench scale may use a CSTR as a preheater with wood)
Carbon efficiency achieved for forest residues

Purge: 52 g (27% of C) (available for CHG which produces a medium Btu gas)

Feed Prep -200µ

HTL Reactor 350°C 200 bar

Filter

Solids 3 g

Separation

bio-crude 35 g (61% of C)

Hydrotreater 138 bar

Gas 10 g

H₂ 1 g

Gas 1 g

Hydrocarbon Product 30 g (60% of C)

Aqueous 5 g

Basis: 100 g Pine forest residue

<table>
<thead>
<tr>
<th>Step</th>
<th>Carbon Efficiency†</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTL biocrude yield</td>
<td>61%</td>
</tr>
<tr>
<td>Hydrotreating yield</td>
<td>96%</td>
</tr>
<tr>
<td>Combined</td>
<td>59%</td>
</tr>
</tbody>
</table>
Upgrading via hydrotreatment results

**HTL bio-crude upgrading**
- 70 h test
- One of 4 conditions
- Excellent mass/carbon balances
- Very high de-oxygenation and TAN reduction

### Parameter Table

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Balance</td>
<td>%</td>
<td>101</td>
</tr>
<tr>
<td>Carbon Balance</td>
<td>%</td>
<td>99.8</td>
</tr>
<tr>
<td>Oil Yield</td>
<td>g dry/g dry feed</td>
<td>0.85</td>
</tr>
<tr>
<td>Carbon Yield</td>
<td>g C/g C in feed</td>
<td>0.96</td>
</tr>
<tr>
<td>Gas Yield</td>
<td>g gas/g dry feed</td>
<td>0.034</td>
</tr>
<tr>
<td>Produced Water Yield</td>
<td>g produced water per g dry feed</td>
<td>0.16</td>
</tr>
<tr>
<td>H₂ consumption</td>
<td>g H₂/100g dry feed</td>
<td>3.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>bio-crude</th>
<th>Upgraded</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/C ratio</td>
<td>dry basis</td>
<td>1.14</td>
<td>1.36</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Wt% dry</td>
<td>14</td>
<td>0.009</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>ppm</td>
<td>3800</td>
<td>520</td>
</tr>
<tr>
<td>Sulfur</td>
<td>ppm</td>
<td>650</td>
<td>19</td>
</tr>
<tr>
<td>Oil density</td>
<td>g/ml</td>
<td>1.13</td>
<td>0.912</td>
</tr>
<tr>
<td>Moisture</td>
<td>Wt%</td>
<td>13</td>
<td>0.35</td>
</tr>
<tr>
<td>TAN</td>
<td>mg KOH/g</td>
<td>140*</td>
<td>0.76</td>
</tr>
</tbody>
</table>

* TAN anomaly; HTL biocrude TAN is typically 40
Hydrothermal liquefaction – is suitable for a broad range of wet feedstocks

- Algae Paste
- Algae HTL Oil
- Hydrotreated Algae HTL Oil
- Wood Paste
- Wood HTL Oil
- Hydrotreated Wood HTL Oil
## Hydroprocessing of HTL algae biocrude

<table>
<thead>
<tr>
<th>Hydrotreatment</th>
<th>Low lipid</th>
<th>High lipid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalyst bed temperature, °C</strong></td>
<td>105-400</td>
<td></td>
</tr>
<tr>
<td><strong>Space velocity, L/L/hr</strong></td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td><strong>H₂ Feed: L/h @ 2000 psig</strong></td>
<td>85</td>
<td></td>
</tr>
<tr>
<td><strong>H₂ Consumption, g/100g feed</strong></td>
<td>2.6-3.8</td>
<td></td>
</tr>
<tr>
<td><strong>Mass balance</strong></td>
<td>91-98%</td>
<td></td>
</tr>
<tr>
<td><strong>Oil yield, L/L bio-oil</strong></td>
<td>0.8 – 0.94</td>
<td></td>
</tr>
</tbody>
</table>

### Bio-oil Product Composition, dry weight basis

- **Carbon, Wt%**: 84-85%
- **Hydrogen, Wt%**: 13.5%
- **Oxygen, Wt%**: 1.2-1.8%
- **Nitrogen, Wt%**: 0.08-0.25%
- **Sulfur, Wt%**: <0.005%

**Process low lipid algae, high lipid algae, cyanobacteria…**

Data shown from early work prior to optimizing hydrotreating for HTL biocrude

**Catalyst**: sulfided CoMo on alumina

**Observation**: No catalyst performance degradation

**TAN <0.1-0.2**

Maintain paraffin (without aromatizing)
Upgraded HTL biocrude from algae: 85% diesel (paraffinic) (NAABBB: Solix, Cellana and TAMU)
Moving forward

- Commissioning 1,000 L/day (20wt% BDAF) continuous HTL/CHG system for algal feedstock; NAABBB-Reliance-PNNL-Genifuel Hydrothermal System 2014
- Waste sludge R&D starting in FY15 (Genifuel/ Water Environment Research Foundation)
Today will focus on production of jet fuel from ethanol feedstock.

Also used as a means to improve quality of fast pyrolysis bio-oils at PNNL.

Using alkylation technology from refinery to make high quality fuels.

Figure Courtesy of NABC
LanzaTech – Recycling carbon for production of alcohol

- Industrial Waste Gas: Steel, PVC, Ferroalloys
- Natural Gas, CH₄: Associated Gas, Biogas
- Solid Waste: Industrial, MSW, DSW
- Inorganic CO₂

Gas Fermentation

- Reforming: CO → CO + H₂
- Gasification: CO + H₂ + CO₂
- Renew-able H₂: CO₂ + H₂
- Renewable Energy: CO₂ + H₂O + e- → CO + H₂

Fuels
Chemicals

Source: LanzaTech
Alcohol to jet fuel (ATJ)

A novel route to drop-in hydrocarbon fuels through recycling waste carbon

Using refinery alkylation chemistry to build carbon chain to jet fuel
Alcohol to jet

Can make isoparaffins or cyclics dependent on reaction conditions

C4— butanol, i-butanol
- Cobalt, Gevo, et al
- fuel primarily C12 and C16 (limited mol. chains)

C2— ethanol
- Swedish Biofuels (+CO/H$_2$)
- PNNL/Imperium (SPK)
- broad chain length

OH
\[ \text{catalyst} \rightarrow \text{heat} \rightarrow \text{catalyst} \]

1. H$_2$ catalyst
2. Distillation

Dimer (C8)
Trimer (C12)
Tetramer (C16)
Jet fuel production from waste gas

- Multi-thousand hours on stream (catalyst life)
- "Fuel is very stable, wide boiling isoparaffinic kerosene" (C10-C16)
- Exceeds D1655 standards including 325 JFTOT (thermal oxidation), high flashpoint (56°C), low freezing (<-70°C), no gum, "not easy to do"

Take home message:
PNNL's unique conversion technology can produce jet fuel from ethanol, which is widely available in large volumes.
ATJ summary

Jet A, JP-8

Product

- ATJ-SKA (Swedish)
- ATJ-SPK

Feedstock

- Butanol /ethanol
- Cellulosic ethanol
- Gas fermentation

Hydrocarbon mix depends on the technology butanol-producers C8,12 and 16 Ethanol give range of hydrocarbons

Source: Dr. Timothy Edwards, Air Force Research Laboratory
Conclusions

- In the last 2 years we have made tremendous strides addressing challenges in refinery integration

- **FCC operations**
  - Are possible with certain bio-oils co-processed with refinery intermediates—produce gasoline-rich streams

- **Hydrotreating operations**
  - Are required for upgrading bio-oils and also used with biocrudes
  - Pyrolysis/liquefaction lead to cyclic hydrocarbons from wood (unless ring opening is deployed)
  - Hydrogen demand varies by technology, and is significantly reduced with HTL

- **Alklyating operations**
  - Alcohol to jet moves us out of the classical liquefaction paradigm

- **Insertion Point 3 (blendstock)** has the lowest risk

- **Insertion Point 2 (co-processing)** risk remains high
  - Efforts in place to understand value of bio-derived material within the refinery (NREL/PNNL)
Next steps

- Moving HTL biocrude to refinery integration (Note: Sapphire presented on this at the Algal Biomass Organization Conference)
- Rather than offering a petroleum substitute, we are looking where can we provide a value added material to refiners and to OEMs
- Focus of efforts unfolding—New Fuels and Vehicle Co-Optima
Challenge: catalyst bed stability

Deactivation of RuS\textsubscript{x}/C leads to unstable material, which forms "gunk" resulting in reactor plugging in < 100 h.

CoMoS\textsubscript{x}/C also exhibits limitations to its catalyst life and deactivation occurs over <100 h campaign.

Elliott et al. *Energy Fuels* 2012, 26, 3869

<table>
<thead>
<tr>
<th>TOS (h)</th>
<th>Oil Yield (g/g dry feed)</th>
<th>H\textsubscript{2} consumption (L/L feed)</th>
<th>Fuel products</th>
</tr>
</thead>
<tbody>
<tr>
<td>24-50</td>
<td>0.40</td>
<td>444</td>
<td>0.7</td>
</tr>
<tr>
<td>66-82</td>
<td>0.43</td>
<td>342</td>
<td>2.1</td>
</tr>
</tbody>
</table>
6 longer duration runs to generate oil for upgrading

130 h on-stream, 7 L bio-crude

Mean balance: Wood 99% (Mass); 88% (carbon)

Mean balance: Cornstover 96% (Mass); 83% (carbon)
## HTL bio-crude from Cellana algae

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low lipid</th>
<th>High lipid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Velocity, L/L/h</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>350</td>
<td>348</td>
</tr>
<tr>
<td>Mass Balance</td>
<td>102%</td>
<td>97%</td>
</tr>
<tr>
<td>Total Carbon Balance</td>
<td>91%</td>
<td>96%</td>
</tr>
<tr>
<td>Oil Yield, Mass Basis (BD)</td>
<td>65%</td>
<td>64%</td>
</tr>
<tr>
<td>Oil Yield, Carbon Basis</td>
<td>81%</td>
<td>82%</td>
</tr>
<tr>
<td><strong>Bio-Oil Composition, Dry Weight Basis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon, Wt%</td>
<td>77.0%</td>
<td>77.6%</td>
</tr>
<tr>
<td>Hydrogen, Wt%</td>
<td>10.4%</td>
<td>10.6%</td>
</tr>
<tr>
<td>Oxygen, Wt%</td>
<td>8.0%</td>
<td>7.2%</td>
</tr>
<tr>
<td>Nitrogen, Wt%</td>
<td>4.2%</td>
<td>4.0%</td>
</tr>
<tr>
<td>Sulfur, Wt%</td>
<td>0.3%</td>
<td>0.3%</td>
</tr>
</tbody>
</table>

Density = 0.95 g/ml

Algae from Cellana, *Nanno. salina* low and high lipid