Co-Processing of Green Crude in Existing Petroleum Refineries

SOAP-Jet (CAAFI R&D Team) 2.2 Webinar
23 January, 2015, 1-2pm EST
Ben Saydah, Sapphire Energy
Overview of Sapphire’s process for making algae-derived fuel

1. **Strain development**
   - Advanced genetics programs

2. **Cultivation module**
   - Open pond, CO₂, and ag industry crop protection and fertilizers

3. **Harvest module**
   - Proprietary process to flocculate and de-water

4. **Conversion module**
   - High efficiency, proprietary process to produce oil

5. **Oil refining module**
   - Upgraded in a refinery or by a stand-alone processor

6. **Nutrient recycle and residual handling stream**

Harvested water recycle loop

Oil products:
- Jet
- Diesel
- Gasoline

Other products:
- Other
Scalable Technology: Leveraging Existing Techniques and Best Practices from Other Industries

Sapphire is adopting elements of already-scaled and low-cost processes to reduce risk and speed our path to commercialization.

Source: UN FAO; BP statistical review 2012
Scalable Technology: Leveraging Existing Techniques and Best Practices from Other Industries

- **Cultivation**: Rice Paddies
  - 398 million acres under cultivation worldwide

- **Harvest**: Wastewater Treatment Plants
  - 15 trillion gallons per day processed worldwide

- **Conversion**: Thermal Conversion, Solvent Extraction
  - Millions of gallons per day used in a variety of industries

- **Refining**: Petroleum Refining
  - World Refinery capacities in 2011 reached 93,000 kbd

**Sapphire is adopting elements of already-scaled and low-cost processes to reduce risk and speed our path to commercialization**

Source: UN FAO; BP statistical review 2012
Conversion: Proprietary Wet Conversion Process Maximizes Oil Yield & Avoids Costly Drying

Sapphire uses a proprietary, innovative, hydrothermal conversion system that is being scaled up with assistance from Linde.

Concentrated algae enters the converter as a slurry

Slurry undergoes chemical reactions

- **Heat and pressure:** the slurry is exposed to heat and pressure, releasing lipids and converting algae biomass to Green Crude oil.
- **Chemicals:** solvents are added to complete separation process.

Conversion process creates refinable crude oil

Concentrated algae is processed using proprietary technology to convert biomass into oil.
Sapphire Green Crude oil has properties that are similar to a petroleum refinery feedstocks making it attractive for refinery co-processing.

Sapphire Green Crude oil reports a full boiling range in high temperature simulated distillation.

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Sapphire Green Crude oil compared to petroleum crude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling range</td>
<td>Similar</td>
</tr>
<tr>
<td>API Gravity</td>
<td>Similar to a heavy crude oil</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Lower</td>
</tr>
<tr>
<td>Total Acid Number</td>
<td>Similar to high TAN crudes</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>Lower</td>
</tr>
<tr>
<td>Yield of Transportation Fuels</td>
<td>Similar</td>
</tr>
<tr>
<td>Carbon Footprint</td>
<td>Lower</td>
</tr>
<tr>
<td>Nitrogen and Oxygen</td>
<td>Higher</td>
</tr>
<tr>
<td>Metals</td>
<td>Higher</td>
</tr>
</tbody>
</table>
Sapphire has tested of many options for refinery co-processing of Green Crude oil.
Sapphire has tested of many options for refinery co-processing of Green Crude oil
Crude blending – why does it matter?

Incompatible crude oils can cause refinery upsets when blended together

- Refiners run multiple crude oils at the same time to optimize overall refinery utilization and maximize profitability
- The co-mingling of incompatible crude oils can cause unplanned refinery outages
  - Mixing incompatible crude oils can lead to heat exchanger fouling and desalter upsets
  - Most crude unit fouling is caused by destabilization of asphaltenes
- Refiners test crude oil compatibility prior to co-processing different crudes
- Baker Hughes Field ASIT Services™ technology is a leading technology to study asphaltene stability in crude blends
Testing using Baker Hughes ASIT™ shows Sapphire Green Crude oil helps to stabilize asphaltenes in petroleum crude oils

- Preliminary blend studies show that blending Green Crude into conventional crude oils has a positive effect on asphaltenes stability
- Coker feed asphaltenes stability increases up to 10% addition of Green Crude but with any higher blend ratios there is a decreasing trend
- Stability of Shale oil, WCS and Bio crude blend was 5x greater than stability of shale oil/ WCS blend alone
Sapphire has tested many options for refinery co-processing of Green Crude oil.
Fluid Catalytic Cracking: converts high molecular weight gasoils to gasoline, distillate and petrochemical feedstock

- Key conversion unit in most US refineries
- Heavy gasoils are converted with a fluidized catalyst to crack the carbon carbon bonds
- Coke is deposited on the catalyst in the reactor and burned off in the regenerator to provide heat to the process
  - Robust process design enables new catalyst to be added without a shutdown
- Cracking lowers the average molecular weight and produces a high yield of gasoline and diesel precursors
- FCC products typically need to be processed downstream to produce transportation fuels
  - C4’s alkylated to improve gasoline anti-knock properties
  - Gasoline and diesel range material hydrotreated to remove sulfur
Sapphire Green Crude has been tested through refinery fluid catalytic cracker at lab scale and will have a higher margin than typical refinery feed

- Product quality from hydrotreating algae Green Crude are consistent with petroleum derived feed
- Products from Fluid Catalytic Cracking algae Green Crude are of higher value than traditional vacuum gasoil feed (VGO)
- Coke formation was the same for petroleum VGO and Green Crude
- Higher nitrogen and oxygen had no impact on yield or product quality
- Higher metals can cause increased catalyst deactivation

<table>
<thead>
<tr>
<th>FCC Conversion</th>
<th>Green Crude compared to petroleum VGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/O</td>
<td>Lower</td>
</tr>
<tr>
<td>Conversion (wt%)</td>
<td>Same</td>
</tr>
<tr>
<td>C2- (wt%)</td>
<td>50% Lower</td>
</tr>
<tr>
<td>C3</td>
<td>30% Higher</td>
</tr>
<tr>
<td>C4</td>
<td>30% Higher</td>
</tr>
<tr>
<td>Gasoline</td>
<td>Lower</td>
</tr>
<tr>
<td>Light Cycle Oil (diesel)</td>
<td>50% Higher</td>
</tr>
<tr>
<td>Decant Oil</td>
<td>75% Lower</td>
</tr>
<tr>
<td>Coke on Catalyst</td>
<td>Same</td>
</tr>
</tbody>
</table>

**NOTE:** FCC yield demonstrated using MAT Testing (ASTM D3907)
Sapphire has tested of many options for refinery co-processing of Green Crude oil.
Hydrotreating: uses hydrogen to remove sulfur from transportation fuels

- Used to remove sulfur from gasoline and diesel range refinery streams
- Found in almost every refinery
- Fixed bed catalytic reaction in the presence of hydrogen at elevated temperature (600 to 900 °F) and pressure (300 to 2500 psi)
- Removes about 95+% of contaminants such as nitrogen, sulfur, oxygen, and metals from liquid petroleum fractions
- Hydrotreating catalyst typically lasts 24 to 48 months and requires a unit shutdown to change out
Diesel from 10% Sapphire Green Crude/ 90% petroleum distillate produced a higher quality product than 100% petroleum distillate feed

- Hydrotreating was done at typical refinery conditions (2000psi) with a commercial hydrotreating catalyst
- Product has lower aromatic content, lower sulfur, higher cetane
- Negligible catalyst deactivation and coking
- Higher feed oxygen and easy to convert nitrogen produced manageable exotherm at 10% feed with no adverse downstream impacts
- 75 to 85 wt% of the algae oil ended up in the diesel product\(^1\)
- 82 to 88 wt% of the algae carbon ended up in the diesel product\(^2\)
- Hydrotreated over 400 gallons of 10% bio-crude blends with no detrimental impact on catalyst

<table>
<thead>
<tr>
<th>Nitrogen is 90+% easy to convert nitriles and amides</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Hydrotreated product quality</th>
<th>100% Petroleum Distillate Feed</th>
<th>10% SEI Green Crude / 90% Petroleum Distillate Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane</td>
<td>56</td>
<td>64</td>
</tr>
<tr>
<td>Sulfur (ppm)</td>
<td>7.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Aromatics (%)</td>
<td>16.4</td>
<td>10.1</td>
</tr>
<tr>
<td>Saturates (%)</td>
<td>80.9</td>
<td>88.3</td>
</tr>
<tr>
<td>Olefins (%)</td>
<td>2.7</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Notes: (1) Based on pilot plant mass balance, (2) Based on C14 carbon dating
Sapphire has tested of many options for refinery co-processing of Green Crude oil
Coking: converts the bottom of the barrel to higher value intermediates

- A coker converts low value high molecular weight vacuum resid to higher value gasoline, jet fuel and diesel blending components
- Coking process can be explained as “Thermal decomposition of high molecular weight hydrocarbon molecules to smaller molecules”
- The principle of coking is simple, requiring only time and temperature
- All the metals and a significant portion of the feed sulphur and nitrogen are rejected in the petroleum coke
- Petroleum coke yield is about 20 to 30 wt% of feed and is essentially solid carbon
  - Cokers produce sponge fuel grade, shot fuel grade or anode grade coke
  - Anode grade coke is sold at a premium while fuel grade is sold at its heating value
Green Crude coker yield is essentially the same as petroleum feed stock and coking provides the lowest risk entry point into a refinery

- Green Crude coker liquid products still contained higher levels of nitrogen and oxygen
- Liquid product yield is the same between Green Crude and petroleum based feed
- Metals were concentrated in petroleum coke
- Green Crude coker product did not adversely effect coke quality

<table>
<thead>
<tr>
<th></th>
<th>Petroleum Feed (wt%)</th>
<th>Green Crude (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Gas / LPG</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>Gasoline Range</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>Diesel Range</td>
<td>19</td>
<td>18</td>
</tr>
<tr>
<td>Gasoil Range</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td>Coke</td>
<td>9</td>
<td>10</td>
</tr>
</tbody>
</table>
Sapphire Green Crude can be inserted into multiple refinery locations generating similar yield and margin to standard petroleum feedstock

- The testing completed to date has produced data to reduce the perceived risk to processing Green Crude by demonstrating:
  - Co-processing Green Crude with petroleum crude reduces the chance of asphaltene deposition
  - FCC has higher transportation fuels yield than petroleum VGO and similar coke laydown
  - High levels of nitrogen in Green Crude are easily removed via hydrotreating
  - 82+% of the carbon in Green Crude ends up in the diesel product after hydrotreating
  - Metals are concentrated in the coke in the coking process and Green Crude yields are similar to petroleum feeds
- Further testing and larger scale testing is required to provide refiners with the confidence needed to process Green Crude in existing refineries

Refinery insertion points have different process risk and margin

Relative Refining Margin

Margin based on 2014 YTD average USGC prices and lab/pilot scale yield data
1. Crude Unit, 2. FCC, 3. Hydrotreater, 4. Coker