FCC Co-Processing: Observations on the Production Method for Low Carbon Fuels

13 December 2016 -- Sacramento, California
UOP Creates Knowledge for the Oil and Gas Industry

UOP technology makes more than 60% of the world’s gasoline, 70% of its polyester and 90% of biodegradable detergents, and processes more than 40% of its LNG.

Better Economics
UOP technologies offer a high return on investment.

Continuous Innovation
Continuous technology improvement allows customer operations to remain cutting edge.

Reliability
UOP technologies are among the most widely proven in the world.

Expertise
UOP has a century-long record leading technology development for the oil and gas industry.

- Process Technology
- Catalysts
- Adsorbents
- Equipment
- Services

2,500 Engineers and scientists

31 out of 36 refining technologies in use today were developed by UOP.

10,000+ Active patents

800+ R&D employees

Largest process licensing organization in the world.

Honeywell UOP
Renewable Fuels from Co-Processing of RTP Biocrude

Utilize existing refinery assets & infrastructure

- Biocrude
- Vacuum Gas Oil (VGO)
- LPG
- Cat Gasoline
- Light Cycle Oil (LCO)
- Main Column Bottoms (MCB)

Partially renewable products sent downstream
Path to Low Carbon Fuels

- Fuels produced from FCC co-processing have one of the lowest CI values under the CA LCFS
- Low CI biofuels are extremely valuable to refineries who must comply with the declining LCFS carbon intensity targets

Ensyn Receives Key Regulatory Approvals From California’s Air Resources Board

Feb 8, 2016  Ensyn has been granted key regulatory approvals by California’s Air Resources Board (ARB). These approvals relate to the application of Ensyn’s Renewable Fuel Oil (RFO™) as a renewable feedstock for refineries in California for the production of renewable gasoline and diesel (Refinery co-processing). The approvals have been granted pursuant to California’s Low Carbon Fuel Standard (LCFS).

The regulatory approvals received from the ARB covers the production of both gasoline and diesel via RFO co-processing in specific CA refineries using RFO produced at Ensyn’s facility in Ontario from forest residues. The carbon intensity of the resulting renewable gasoline and diesel was determined to be in the range of approximately 20-25 g Co2e/MJ, or approximately 70% less than traditional petroleum-base fuels.


Select LCFS Pathway Carbon Intensities (gCO₂e/MJ)
Commercial Status of Technology
UOP Commercial Biocrude Trial

• Conducted in US located FCC unit just prior to T/A

• Purpose:
  - Prove the biocrude injection system in a refinery environment
  - Reveal obvious operational changes due to biocrude addition and look for “show-stoppers” that might preclude a larger-scale / longer duration trial / commercialization strategy
  - Generate FCC products when co-processing for further analysis to look for components of concern in catalysts, liquid hydrocarbon products, and waste water streams

• Conclusions
  - Data and indications show that with proper mitigation measures in place, a long-term biocrude addition trial can take place with minimal risk
  - No “show-stoppers” were observed
Important Fuel Properties
Virtually Unchanged During Commercial Trial

Naphtha

Olefin & Naphthene

- Before RTP Green Fuel added
- 8 hours of RTP Green Fuel Addition
- 16 hours of RTP Green Fuel Addition

Naphtha

Mono-Aromatics by Carbon Number

- Before RTP Green Fuel added
- After 8 hours of RTP Green Fuel Addition
- After 16 hours of RTP Green Fuel Addition

Bulk chemical composition of FCC products similar to petroleum-only feed
Assessing Percent Modern Carbon (pmC) in Co-Processing Products
Sources of Variability in determining fraction of biogenic carbon

\[ \frac{^{14}\text{C}}{^{12}\text{C}} \text{ in Feed} \]

**Abs. Error [pmC]**(*)

-1 to + 2.2

**Comments**

Can be compensated for in analysis

**Processing**

0

**Sampling and analysis**

+/- 3

Various time constants; control dependent

Terrestrial only; unknown for aquatic/terrestrial blends

(*) pmC = percent modern C
Variability in sampling and measuring biogenic carbon fractions

- Sampling and $^{14}$C measurement is standardized through ISO 13833 and ASTM D6866-16.
- Three measurement methods are described. Among these, AMS (accelerator mass spectrometry) shows best accuracy and precision and allows for the $^{13}$C/$^{12}$C correction mentioned above.
- Stated standard deviation is 0.5 percent modern carbon (pmC) on one instrument, for AMS.
- Controlled ASTM inter-lab testing shows error to be +/- 3 pmC (absolute), (with application of natural abundance correction), in the range 8-100 pmC.
  - Data confirmed by Norton and Devlin (2006)$^{(1)}$
- ASTM warns for additional and unquantified error when complex mixtures of aquatic and terrestrial materials are used.

Summary

• FCC co-processing is a technology breakthrough to produce sustainable cellulosic transportation fuels
  - Demonstrated on a commercial scale in US refiner’s FCC unit. Full commercial implementation likely within the next year
  - Provides obligated parties with a pathway to generate and satisfy the EPA cellulosic RVO / RINs
  - Low cost technology revamp solution that can be easily implemented in existing FCC units during next T/A
  - Determination of percent modern carbon (pmC) best done through mass balance within refinery units
Example Refinery RVO and Potential RIN Generation from FCC Co-Processing

<table>
<thead>
<tr>
<th>Annualized Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Crude Processing Rate</td>
<td>250,000</td>
<td>BPSD</td>
</tr>
<tr>
<td>Yield of trans. fuel / barrel crude</td>
<td>0.70</td>
<td>VOL%/VOL%</td>
</tr>
<tr>
<td>Yearly Factor</td>
<td>0.95</td>
<td>Day / Year</td>
</tr>
<tr>
<td>Transportation Fuel Production</td>
<td>2.548</td>
<td>Billion gallons/yr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Incremental 2015 RVO %</th>
<th>Incremental 2016 RVO %</th>
<th>Proposed Incremental 2017 RVO %</th>
<th>Fuel Type</th>
<th>2017 RINs Req’d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.069%</td>
<td>0.128%</td>
<td>0.173%</td>
<td>Cellulosic biofuel (D3, D7)</td>
<td>4,409,100</td>
</tr>
<tr>
<td>1.490%</td>
<td>1.590%</td>
<td>1.670%</td>
<td>Biomass-based Diesel (D4)</td>
<td>42,561,829</td>
</tr>
<tr>
<td>0.061%</td>
<td>0.292%</td>
<td>0.380%</td>
<td>Advanced biofuel (D5)</td>
<td>9,608,269</td>
</tr>
<tr>
<td>7.90%</td>
<td>8.090%</td>
<td>8.220%</td>
<td>Renewable Fuel (D6)</td>
<td>209,495,948</td>
</tr>
<tr>
<td>9.52%</td>
<td>10.10%</td>
<td>10.44%</td>
<td>Total RINs</td>
<td>266,075,145</td>
</tr>
</tbody>
</table>

- Co-processing Biocrude in a 30,000 BPSD at 3 wt% on feed can produce ~9 mil cellulosic RINs

Refinery cellulosic RVO can be met with FCC co-processing