Upgrading of Catalytic Pyrolysis Oil

Steven Gust
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Neste in brief

A refining and marketing company focused on premium-quality traffic fuels

Refining capacity: 15 million t/a of petroleum products and 2 million t/a of renewable diesel

Net sales: €17.5 billion (2013)

Operations in 15 countries; employs approx. 5,000 people

Listed on the Helsinki Stock Exchange

Largest owner: the Finnish State (50.1%)
Porvoo Refinery
Vision: To be the preferred partner for cleaner traffic fuel solutions.
Neste presence globally

**Production:**
- Porvoo
- Naantali
- Rotterdam
- Singapore
- Nynäshamn
- Bahrain (joint venture, Neste's share 45%)

**Sales and marketing:**
- Espoo
- Stockholm
- Tallinn
- Riga
- Vilnius
- St. Petersburg
- Geneva
- Beringen
- Houston
- Toronto
- Dubai
- Singapore

Headquarters: Espoo
Development of Cleaner Products

- **80-90**
  - Lead-free city-gasolines

- **2007**
  - Renewable NExBTL diesel

- **2008**
  - Less sulfur-free fuels
  - VHVI base oils

- **2010**
  - Neste Green diesel: 10% renewable NExBTL diesel

- **2011**
  - Neste Green 100: 100% renewable NExBTL diesel
  - Renewable NExBTL aviation fuel

- **2012**
  - Neste Pro Diesel: 15% renewable diesel
  - WWFC specification – the best diesel recommended by the world’s car manufacturers
  - NExBTL Renewable naphtha

June 5, 2015
World’s largest producer of renewable diesel

- Premium-quality NEXBTL provides high performance with a lower carbon footprint.
- Use sustainable raw materials
- Customers include corporate customers in Europe and North America.
- Increasing production capacity to 2.6 million tons by the end of 2016.
NEXBTL Commercialization Pathway

- The 1st patent application
  - No prerequisite yet for commercial use
- R&D project to develop use of biofeedstocks in refining
- R&D restarted due to preparation of the Biofuel directive in the EU
- The 1st patent application
- Process modeling completed
- Basic design of a NExBTL unit commenced
- Commercial development of technology by Neste Oil R&D and Neste Jacobs
- 1st investment decision to a NExBTL plant
- 1st plant started up at Porvoo
- 2nd plant under construction
- Investment decision to build a 800,000 t/a plant in Singapore
- The 2nd plant started up at Porvoo
- Investment decision to build a 800,000 t/a plant to Rotterdam
- 1st plant started up at Porvoo
- 2nd plant under construction
- Investment decision to build a 800,000 t/a plant
- The 2nd plant started up at Porvoo
- 2008
- 2009
- June 5, 2015

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Expanding the feedstock portfolio

- Waste animal fat
- Waste fish fat
- Palm oil fatty acid distillate (PFAD) and stearin
- Technical corn oil
- Tall oil pitch
- Palm oil
- Camelina oil
- Jatropha oil
- Soybean oil
- Rapeseed oil

Neste Oil uses also bioethanol obtained from global markets as biocomponent in 95 E10 and 98 E5 gasolines
NEXBTL products

- NEXBTL renewable diesel
- NEXBTL renewable aviation fuel
- NEXBTL renewable naphtha and propane
- NEXBTL renewable isoalkane
BioBoost
This project has received funding from the European Union’s Seventh Programme for research, technological development and demonstration under grant agreement No 282873
Neste’s Role in BioBoost

Straw, agri-residues
Organic waste & residues
Wood & forest residues

Fast pyrolysis
Hydrothermal carbonisation
Catalytic pyrolysis

By-products of pyrolysis and HTC

WP 4: Transport, logistic and safety concept for energy carrier(s)

Special chemicals
Gasification & synthesis
Heat & power
Refinery

WP 6: Technical, economic and sustainability assessment of complete chain concepts

Neste

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5.3.1 Evaluation of catalytic pyrolysis oil and selection of reaction

5.3.2 Reactor tests for hydrotreating or catalytic cracking of catalytic pyrolysis oil

5.3.3 Evaluation of different energy carriers, especially catalytic pyrolysis oil, as a feedstock of NESTE Oil refineries
Our tools:

- **PARR autoclave stirred batch reactor (90 ml)**
  - 3 g catalyst in a wire mesh basket
  - 50 g feed / test

- **Continuous flow tubular reactor (tube volume 50 ml)**
  - 24 g catalyst diluted with inert SiC 1:1
  - 800 g feed / ~ 6 days

+ lots of analyses
## Typical Results

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Ident2</th>
<th>Ident6</th>
<th>Ident8</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Run time</strong></td>
<td>h</td>
<td>25.8</td>
<td>94.7</td>
<td>118.1</td>
</tr>
<tr>
<td><strong>Average T</strong></td>
<td>C</td>
<td>298</td>
<td>299</td>
<td>299</td>
</tr>
<tr>
<td><strong>Maximum T</strong></td>
<td>C</td>
<td>352</td>
<td>353</td>
<td>353</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>bar</td>
<td>148</td>
<td>148</td>
<td>140</td>
</tr>
<tr>
<td><strong>WHHSV</strong></td>
<td>h⁻¹</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
<td>l/h</td>
<td>12.4</td>
<td>13.7</td>
<td>13.7</td>
</tr>
<tr>
<td><strong>Oil sample, wet</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>MCR</strong></td>
<td>wt-%</td>
<td>16.8</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td><strong>Density at 15 C</strong></td>
<td>kg/m³</td>
<td>1.18</td>
<td>871</td>
<td>889</td>
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<tr>
<td><strong>Viscosity at 20 C</strong></td>
<td>mm²/s</td>
<td>2.4</td>
<td>2.9</td>
<td>2.7</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td>wt-%</td>
<td>5.0</td>
<td>0.01</td>
<td>0.043</td>
</tr>
<tr>
<td><strong>Oil sample, dry</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>H</strong></td>
<td>wt-%</td>
<td>7.1</td>
<td>12.4</td>
<td>11.5</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>wt-%</td>
<td>76.1</td>
<td>86.2</td>
<td>85.4</td>
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<tr>
<td><strong>N</strong></td>
<td>wt-%</td>
<td>0.065</td>
<td>0.001</td>
<td>0.015</td>
</tr>
<tr>
<td><strong>O, calculated</strong></td>
<td>wt-%</td>
<td>16.8</td>
<td>1.4</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>H/C</strong></td>
<td>mol/mol</td>
<td>1.11</td>
<td>1.71</td>
<td>1.60</td>
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<tr>
<td><strong>O/C</strong></td>
<td>mol/mol</td>
<td>0.17</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td><strong>Degree of HDO</strong></td>
<td>%</td>
<td>94</td>
<td>86</td>
<td>93</td>
</tr>
<tr>
<td><strong>Degree of HDN</strong></td>
<td>%</td>
<td>99</td>
<td>86</td>
<td>86</td>
</tr>
</tbody>
</table>
Experimental Results Summary

- Oil product yield was approximately 73 wt%.
- Hydrogen consumption (based on dry CP oil feed) was 6 wt%.
- Non-condensable gases (13 wt%) primarily paraffinic hydrocarbons.
- CP oil feed requires a stabilization step; catalyst coking could not be prevented.
- Under the operation conditions used, we were not able to remove all oxygen.
Choice of Concept
CP OIL Upgrading Criteria

1. chemical and physical composition
2. miscibility with hydrocarbons
3. tendency to coke
4. EU legislation
5. isolation of products
6. availability of oil refinery units
two stage hydrotreating:
1st stage stabilization, 2nd stage hydrodeoxygenation

separate units but integrated into refinery infrastructure utilizing refinery hydrogen, power and steam and waste water

3rd stage possibly required
CPO Upgrader
Proposed Concept

CPO feed → steam

200-280°C
80-180 bar

C1-C5 gases
steam / hydrogen production

CO₂ out

water

light gases

330-380°C
150 – 200 bar

HRSG

steam

C6-C10

C11-C20

H₂ production

CH₄

SMR

recycle hydrogen

steam

steam
Lessons Learned

1. CP oil is aromatic so processes with hydrogen added are preferred from a yield standpoint
2. much simpler / easier to upgrade CP oil than TP oil based on our results compared to TP upgrading in literature
3. stabilization is required to prevent coking on catalyst; optimum conditions not yet found
4. hydrogen consumption is moderate and could be produced (at least partially) from off gases
5. catalysts did show coking after 3-4 days so conditions (T, H₂ pressure, catalyst etc.) must be further optimized
6. in order to design a commercial process further upgrading studies are required
Neste Conclusions to Date

1. Reactive components are present in CP oil which will require stabilization step
2. Once adequate conditions were found, it was quite easy to upgrade the CP oil.
3. Coking of catalysts occurred even with stabilization indictating that optimum conditions have not yet been found
4. Conclusions are preliminary as no long term (> 3 months) catalyst testing could be performed within the BioBoost project
5. Fuel quality issues remain to be answered
6. It should be possible to resolve these issues provided sufficient CP oil is available for testing