Production of advanced biofuels:
Co-refining upgraded pyrolysis oil

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C. Geantet, G. Toussaint (IRCELYON)
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- Introduction
  - Energy scenario
  - Co-refining pyrolysis oil (BIOCOUP concept)
  - Advanced bio-fuels, advantages co-refining
  - Biomass route

- Pyrolysis oil upgrading – Hydrodeoxygenation
  - Product yields/properties

- Co-refining upgraded pyrolysis oil

- Conclusions
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Energy scenario

- Expected increase in bio-fuels demand

Ref: Shell energy scenarios to 2050 (Shell International BV, 2008)
Co-refining pyrolysis oil
Biomass route

Ligno-cellulosic Biomass (waste) → Pyrolysis oil

Pyrolysis
- 400-550 ºC
- 2 seconds
- Inert atmosphere
- Oil yield: 60-70 wt.%
- Energy yield: ~60-70%

Upgrading
- Hydrodeoxygenation
- Reduction Oxygen and Water content
- Improve miscibility fossil fuel
- Reduce acidity...

Refinery
Co-refining
Advanced bio-fuels

- Contribute to secure the supply of fuels
- The reduction of green-house-gas emissions

- Do *not* compete with the food chain
- Produced from a wider range of ligno-cellulosic biomass
  - agricultural waste,
  - wood,
  - forest residues
  - ...
Advantages of co-refining upgraded pyrolysis oil

- The use of *decentralised pyrolysis plants* that can be near the biomass production site. This means that *only the oil is transported*, reducing transportation costs due to the increase of the volumetric energy of the oil compared to the original biomass.

- After pyrolysis, large part of the *minerals from biomass* is not transferred to the oil but *remain as ash*. Thus, pyrolysis oil contains *less inorganic material* that could poison subsequent catalytic processes. Moreover, the ash can be returned to the soil as *fertiliser*.

- As the *upgrading plant* would be next to (or inside) the *refinery*, all the necessary *utilities* would be already available and the product obtained after co-refining could use the *existing distribution network*.
Is co-refining possible?

- What should the upgrading severity be?
  - How much oxygen removal?
  - How much hydrogen is needed for upgrading?

- In which refinery unit should the oil be co-refined?
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Upgrading treatment – Hydrodeoxygenation (HDO)

- Active catalyst (Ru/C)
- High $\text{H}_2$ pressure
- Long residence time (>4h)
- 200-400 °C, >200 bar.
- Batch autoclave 5L
Upgrading Products

Pyrolysis oil + H₂ → HDO
Final T: 230-340 °C
P: 290 bar

Oil Phase
- dry yield: 47-50 wt.%
- Energy yield: 55-68 %
  (MJ HDO oil / MJ PO+H₂)

Aqueous Phase
- dry yield: 39-14 wt.%

Gas Phase
- dry yield: 3-9 wt.%

Produced water
- dry yield: 9-19 wt.%

## Oil properties and H$_2$ consumption

<table>
<thead>
<tr>
<th></th>
<th>Feed oil</th>
<th>HDO oils</th>
<th>Gasoline*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C dry (wt.%)</td>
<td>54</td>
<td>63-74</td>
<td>86-89</td>
</tr>
<tr>
<td>H dry (wt.%)</td>
<td>7</td>
<td>9-10</td>
<td>14-11</td>
</tr>
<tr>
<td>O dry (wt.%)</td>
<td>39</td>
<td>28-16</td>
<td>0</td>
</tr>
<tr>
<td>Water (wt.%)</td>
<td>25</td>
<td>16-2</td>
<td>0</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>17</td>
<td>25-35</td>
<td>~46</td>
</tr>
<tr>
<td>Cocking tendency</td>
<td>27</td>
<td>14-2</td>
<td>~0</td>
</tr>
<tr>
<td>(dry MCRT, wt.%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*estimated values

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>230</th>
<th>260</th>
<th>300</th>
<th>330</th>
<th>340</th>
</tr>
</thead>
<tbody>
<tr>
<td>NL H$_2$/kg feed oil</td>
<td>232</td>
<td>237</td>
<td>290</td>
<td>297</td>
<td>326</td>
</tr>
<tr>
<td>NL H$_2$/MJ of product</td>
<td>21.6</td>
<td>22.0</td>
<td>22.3</td>
<td>21.8</td>
<td>23.6</td>
</tr>
</tbody>
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Where should HDO oil be co-refined?

- Two refinery units have been evaluated
  - Fluid catalytic cracking (FCC)
    - Used to treat heavy refinery feedstocks to lighter more useful fractions such as gasoline, LCO,…
    - Upgraded pyrolysis oil contains heavy molecules
  - Hydrodesulphurisation
    - Used to remove sulphur from fossil fuel to meet environmental specifications
    - Similar to HDO process
Catalytic cracking

- Lab-scale FCC reactor – MAT-5000 - 520 °C
- Equilibrium catalyst from Shell’s FCC units
- Co-refining 20 wt.% HDO oils + 80 wt.% Long Residue
- Complete solubility
- Successful processing without plugging of lines
- Product near oxygen free (some phenolics remaining)
- Product analysed by true boiling point fractions
Co-refining product yields

- Almost all oxygen is transferred to water
- Product yields (corrected by water production) independent of HDO severity

Influence of blending

- Coke yields much higher when HDO oil processed undiluted
- Hydrogen transfer from long residue required for good product distribution
Quality parameters

\[ H/C_{eff} = (H - 2\times O)/C \]

O dry (wt.%)
MCRT (wt.%)
MCRT blend (wt.%)

H/C_{eff} blend
H/C_{eff} blend
H/C_{eff}

230 °C 260 °C 300 °C 330 °C 340 °C
# Biomass route

<table>
<thead>
<tr>
<th></th>
<th>Biomass</th>
<th>Pyrolysis oil</th>
<th>HDO oil</th>
<th>Gasoline, LPG &amp; LCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (g)</td>
<td>100</td>
<td>65</td>
<td>26</td>
<td>20</td>
</tr>
<tr>
<td>Average yields (%)</td>
<td>65</td>
<td>40</td>
<td>75</td>
<td></td>
</tr>
</tbody>
</table>

1.5 g H2 / 100 g biomass

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<th>HDO oil</th>
<th>Gasoline, LPG &amp; LCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (g)</td>
<td>100</td>
<td>61</td>
<td>38</td>
<td>32</td>
</tr>
<tr>
<td>Average yields (%)</td>
<td>61</td>
<td>63</td>
<td>85</td>
<td></td>
</tr>
</tbody>
</table>
Hydrodesulphurisation unit (HDS)

- Lab-scale HDS reactor – Co-refining model compounds


- Competition HDS/HDO was observed, specially at low temperature
Hydrodesulphurisation unit (HDS)

- Lab-scale HDS reactor – Co-refining HDO oils

- SRGO/HDO oil/i-propanol
  - 80/10/10

- 360 °C, 4 MPa, LHSV 2h⁻¹

- HDS/HDO competition using standard HDS catalyst

- Initial catalyst activity recovered after co-processing

C. Geantet, G. Toussaint, L. Braconnier, C. Mirodatos, F. De Miguel Mercader, J. A. Hogendoorn et al. (IRCELYON and University of Twente): Co-processing of SRGO and hydrotreated bio-oils. The 5th International symposium of molecular aspects of catalysis by sulphides (MACS V). 30 May to 3 June 2010. Copenhagen
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- Increasing HDO severity
  - Increases carbon/energy recovery
  - Reduces oxygen and water content

- Successful catalytic cracking co-refining of HDO oil (with high oxygen content) with Long Residue
- Gasoline, LCO and LPG yields remain similar to reference
- The presence of fossil feed appears to be very important

- HDS inhibition is detected for certain oxygenated model compounds and for HDO oils
- Tailoring of co-refining in HDS unit needed to maintain desulphurisation and obtain complete deoxygenation
Acknowledgments

- All BIOCOUP partners

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Thank you for your attention!