Technical Information Exchange on Pyrolysis Oil: Potential for a renewable heating oil substitution

Challenge # 3 – Operational Issues

What are the most significant barriers to overcome in each market segment?
Challenges – Operational Issues

The challenge is to identify the technical knowledge gaps that need to be closed in order for industry to establish the infrastructure to address wide-spread utilization of pyrolysis oils:
- compatibility (blending) with existing hydrocarbon fuels
- long term storage stability
- containment, handling and corrosivity
- fouling and plugging
- burner design and combustion performance

Aside from the knowledge gaps, infrastructure-related requirements and/or regulations must also be addressed:
- technical standards including WHMIS issues: hazard identification and product classification, labelling, material safety data sheets, and worker training and education.
- spillage and emissions monitoring/regulations
- government incentives for infrastructure development
Stability can be addressed by adapting the chemistry of the molecular fragments in the initial pyrolysis step e.g. vapour phase catalysis, removal of polymerization inducing “materials” e.g. ultra-filtration, upgrading of pyrolysis oil to a stable intermediate or hydrocarbon fuel. On the other hand, stabilization can also be addressed by blending with a solvent e.g. alcohol.

Is stabilization required for a heating fuel substitution application? Which approach best lends itself to this end-use? Upgrading? Blending? Fractionation?
Coking in Supply Line Due to Overheating of Bio-oil
Challenges – Combustion

- Combustion of pyrolysis oils by co-firing has been successfully demonstrated at a number of laboratories and industrial sites. A number of labs have also demonstrated combustion of filtered, diluted (usually with alcohol) pyrolysis oils in burners, internal combustion and Stirling engines. There is limited experience in combustion of “untreated” undiluted pyrolysis oil. In the latter area, ignition, control and especially “cold start performance” have been identified as requiring further research.

- Should further combustion research focus on pure pyrolysis oils? What are the critical research needs in combustion? Scale? To what extent is blending of pyrolysis oil acceptable? Required? With which conventional fuel is blending best accomplished? Is emulsification with diesel fuel a suitable approach?
Pyrolysis Oil Combustion Research

Fernando Preto  Natural Resources Canada
CanmetENERGY Research Tunnel Furnace

ONE SEGMENT OF FURNACE
CALORIMETRIC SECTION
28 IN TOTAL

TO FLOW METER

SECONDARY AIR

COOLANT IN

PRIMARY AIR

SWIRL GENERATOR

ADIABATIC SECTION (REFRACTORY)

QUARL

OBSERVATION PORT

PROBE PORTS
## Pyrolysis Oil Analyses

<table>
<thead>
<tr>
<th>Bio-oil</th>
<th>Water Content (wt%)</th>
<th>Viscosity @ 70°C (cSt)</th>
<th>Density @ 25°C (g/cm³)</th>
<th>Acid Content (weak) dry wt%</th>
<th>HHV (MJ/kg)</th>
<th>THF Insolubles (wt%)</th>
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<tbody>
<tr>
<td>Tote 1(#1)</td>
<td>24.96</td>
<td>16.97</td>
<td>1.32</td>
<td>7.40</td>
<td>17.18</td>
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<td>Tote 2(#2)</td>
<td>31.17</td>
<td>4.86</td>
<td>1.20</td>
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<td>14.63</td>
<td>0.80</td>
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</table>

<table>
<thead>
<tr>
<th>Bio-oil</th>
<th>Viscosity @ 40°C (cSt)</th>
<th>Density @ 15°C (g/cm³)</th>
<th>C, wt%</th>
<th>H, wt%</th>
<th>N, wt%</th>
<th>S, wt%</th>
<th>As h wt %</th>
<th>HHV MJ/kg</th>
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<tr>
<td>#1</td>
<td>510.3</td>
<td>1.25</td>
<td>47.12</td>
<td>7.78</td>
<td>0.23</td>
<td>&lt; 0.05</td>
<td>.06</td>
<td>18.97</td>
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<td>#2</td>
<td>817.3</td>
<td>1.27</td>
<td>52.0</td>
<td>6.78</td>
<td>0.23</td>
<td>&lt; 0.05</td>
<td>.70</td>
<td>20.91</td>
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</table>
Variation In Bio-oil Properties In Some Cases Required Nozzle Adjustments
Radiation Flux Measurements

![Graph showing radiation flux measurements for different fuel compositions over distance from burner, in W/cm².]

- #1 Bio-oil
- 65%#1+35%NG
- #2 Bio-oil
- 65%#2+35%NG
- 100 NG

**Distance from Burner, m**

**QIR, W/cm²**

0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00

1 1.5 2 2.5 3 3.5 3.5
#1 Bio-oil combustion results

<table>
<thead>
<tr>
<th>Name</th>
<th>Unit</th>
<th>100% #1 (1)</th>
<th>100% #1 (2)</th>
<th>65% #1</th>
<th>90% #1</th>
<th>80% #1</th>
<th>50% #1</th>
<th>100% NG</th>
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<tbody>
<tr>
<td>Bio oil Feed rate</td>
<td>Kg/h</td>
<td>68.1</td>
<td>68.1</td>
<td>44.3</td>
<td>61.3</td>
<td>54.5</td>
<td>34</td>
<td>0</td>
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<tr>
<td>Oil temp.</td>
<td>C</td>
<td>53.3</td>
<td>50</td>
<td>53.5</td>
<td>53.4</td>
<td>50.4</td>
<td>52.9</td>
<td>0</td>
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<tr>
<td>NG Feed rate</td>
<td>Kg/h</td>
<td>0</td>
<td>0</td>
<td>7.7</td>
<td>2.2</td>
<td>4.4</td>
<td>11</td>
<td>22</td>
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<tr>
<td>Heat input</td>
<td>MJ/h</td>
<td>1292</td>
<td>1292</td>
<td>1250</td>
<td>1280</td>
<td>1268</td>
<td>1230</td>
<td>1170</td>
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<td>Atomising Air Flow rate</td>
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<td>690.1</td>
<td>684.1</td>
<td>652.1</td>
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<td>Stack gas, O2 %</td>
<td>%</td>
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<td>4.55</td>
<td>4.54</td>
<td>4.54</td>
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<td>Stack gas, CO Ppm</td>
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<td>78</td>
<td>47</td>
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## #2 Bio-oil combustion results

<table>
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<tr>
<th>Name</th>
<th>Unit</th>
<th>100% #2</th>
<th>65% #2</th>
<th>90% * #2</th>
<th>90% #2</th>
<th>80% #2</th>
<th>50% #2</th>
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</thead>
<tbody>
<tr>
<td>Bio oil Feed rate</td>
<td>Kg/h</td>
<td>80</td>
<td>52</td>
<td>72</td>
<td>72</td>
<td>64</td>
<td>40</td>
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<td>Oil temp.</td>
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<td>50.8</td>
<td>48.8</td>
<td>52.6</td>
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<tr>
<td>NG Feed rate</td>
<td>Kg/h</td>
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<td>7.7</td>
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<td>2.2</td>
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<td>Heat input</td>
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<td>1673</td>
<td>1497</td>
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<td>Kg/h</td>
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<td>44.5</td>
<td>86.6</td>
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<tr>
<td>Stack gas, O2</td>
<td>%</td>
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<td>4.05</td>
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<tr>
<td>Stack gas, NO</td>
<td>Ppm</td>
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<td>152</td>
<td>141</td>
<td>144</td>
<td>151</td>
<td>122</td>
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<tr>
<td>Stack gas, PM</td>
<td>Mg/m³</td>
<td>242</td>
<td>182</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</table>
Effect of #1 Bio-oil Temperature on CO and NOx

CO and NOx emission variation due to Oil Temperature of the Blend (65% #1, 35% NG)
Effect of Combustion Air Temperature

(1) Tote #1 comb air temp 117°C

(2) Tote #1 comb air temp 46°C
Effect of Bio-Oil Temperature

Bio-oil (#1) Temperature

54°C
45°C

Co-firing with 35% Natural Gas
Cold Start Attempts (Bio-oil #2)

Using Ignitor (Comb. Air Temperature 30C abd 85C)

Natural Gas pilot support – flame extinguished within 1 minute
District Heating with Bio-oil?
Commercial Combustion of Bio-oil

- Project objective
  - Develop automated stand-alone system for bio-oil combustion as replacement for oil/natural gas boilers

- Partners
  - CanmetENERGY
    - Combustion Expertise incl. bio-oil
  - Ensyn Technologies
    - Production & handling of bio-oil oil
  - Brais, Malouin and Associates
    - Power boiler, petrochem and modeling expertise
Facility Development
Further Development

- Nozzle design
- Controls incl. flame sensor location
- Ignition Control
- Flame stability
- Cold Start
Challenges – Corrosivity

- Corrosion studies at ORNL have shown that raw pyrolysis oil is very corrosive to carbon steel and other alloys with relatively low chromium content. Stress corrosion cracking samples of carbon steel and several low alloy steels developed through-wall cracks after a few hundred hours of exposure at 50°C. Chemical analyses have identified the carboxylic acid compounds as well as the other organic components which are primarily aromatic hydrocarbons.

- Are further corrosion studies necessary or is it enough to specify plastic or stainless? Can pyrolysis oil be effectively neutralized?
Challenges – Comfort and Toxicity

- If pyrolysis oils is going to be used for wide-spread heating issues like comfort and toxicity will have to be addressed. Further work is required to develop procedures for dealing with spills. Detailed toxicological data is required for exposure to liquids and vapours. A number of MSDS for pyrolysis oils are available, however the experiences and claims from commercial producers need to be assessed and incorporated into a comprehensive MSDS.

- How can spills be remediated?
  Is there a procedure for resolving MSDS conflicts?
Challenges – Standards and Regulations

- The IEA Bioenergy Task 34 collaboration has development of norms and standards including establishment of standards for bio-oil utilization. Included in this is having a CAS number issued for fast pyrolysis bio-oil (RN 1207435-39-9) and supporting an Ensyn-led effort to develop ASTM Standard D7544-09.

- **What additional standards are required for infrastructure development? Are there local regulatory requirements which must be met?**
IEA Bioenergy Task 34 is evaluating Pyrolysis Oil Designations:

E.G.  
Grade B: Bio-oil for power prod. in medium speed stationary diesel engines TAN <15
Grade D: Light fuel oil (<0.2 wt% solids and ash <0.1%)
Grade G: Heavy fuel Oils (ASTM D7544)
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