Stability of fast pyrolysis oils: comparison of assessment methods

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Introduction
Materials and methods
Results
Conclusions
Fast pyrolysis of biomass for fuels/chemicals

- **Fast pyrolysis**: rapid thermal decomposition of biomass at temperatures ca. 500 °C in the absence of oxygen to produce bio-oil as main product.
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<table>
<thead>
<tr>
<th>Analysis</th>
<th>Pyrolysis oil(^1)</th>
<th>LFO (Tempera 15)(^2)</th>
<th>HFO 180 / 420(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, wt %</td>
<td>15 – 35</td>
<td>0.025</td>
<td>0</td>
</tr>
<tr>
<td>Solids, wt %</td>
<td>0.01 – 1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ash, wt %</td>
<td>0.01 – 0.2</td>
<td>0.01 max</td>
<td>0.08 max</td>
</tr>
<tr>
<td>Nitrogen, wt %</td>
<td>0 – 0.4</td>
<td>0</td>
<td>0.4</td>
</tr>
<tr>
<td>Sulfur, wt %</td>
<td>0 – 0.05</td>
<td>0.2</td>
<td>1.0 max</td>
</tr>
<tr>
<td><strong>Stability</strong></td>
<td><strong>Unstable</strong></td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>Viscosity (40 °C), cSt</td>
<td>15 – 35</td>
<td>3.0 – 7.5</td>
<td>180 / 420 max @50 °C</td>
</tr>
<tr>
<td>Density (15 °C), kg/dm(^3)</td>
<td>1.10 – 1.30</td>
<td>0.89</td>
<td>0.99 / 0.995 max</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>40 – 110</td>
<td>60 min</td>
<td>65 min</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>-9 to -36</td>
<td>-15</td>
<td>15 max</td>
</tr>
<tr>
<td>LHV, MJ/kg</td>
<td>13 – 18</td>
<td>40.3</td>
<td>40.6 min</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>2 – 3</td>
<td>Neutral</td>
<td></td>
</tr>
<tr>
<td><strong>Distillability</strong></td>
<td><strong>Not distillable</strong></td>
<td>Distillable</td>
<td>Distillable</td>
</tr>
</tbody>
</table>

Chemical composition of fast pyrolysis bio-oils

Holocellulose degradation products in bio-oil

Milne T.A. et al., 1997, Developments in Thermal Biomass Conversion
Chemical composition of fast pyrolysis bio-oils

Lignin degradation products in bio-oil

Milne T.A. et al., 1997, Developments in Thermal Biomass Conversion
Stability of fast pyrolysis bio-oils: Aging phenomena

- Aging: polymerization reactions of reactive components in bio-oil to reach equilibrium
- Change of physicochemical properties of bio-oil during storage
- Increase in molecular weight, viscosity and water-insoluble content of bio-oil.
- An exothermic process

Suggested reactions occurring during bio-oil aging\(^1\).

Stability of fast pyrolysis bio-oils: Assessment methods

Viscosity-increase based method

Average molecular weight-increase based method

Carbonyl content based method

Oasmaa et al. 2011, Energy Fuels, 25, 3307–3313

Kim et al. 2015, ChemSusChem, 8, 894 – 900

Oasmaa et al. 2011, Energy Fuels, 25, 3307–3313
Stability of fast pyrolysis bio-oils: Assessment methods

- Stability of bio-oils are usually assessed by viscosity increase based method. It has been a subject of a recent round robin study.
- There were still some variations in the stability assessment results.
Micro carbon residue test for stability assessment

- Originally developed to measure the coking tendency of a petroleum product.
- High molecular weight, oxygenated compounds result in higher micro-carbon residue.
- Research question: Can MCRT be used as a parameter to assess the stability of fast pyrolysis bio-oils?
Introduction
Materials and methods
Results
Conclusions
## Fast pyrolysis oils used in this work

<table>
<thead>
<tr>
<th></th>
<th>Bio-oil #1 (UGent)</th>
<th>Bio-oil #2 (BTG)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reactor</strong></td>
<td>Auger</td>
<td>Rotating cone</td>
</tr>
<tr>
<td><strong>Feedstock</strong></td>
<td>Pine wood</td>
<td>Pine wood</td>
</tr>
<tr>
<td><strong>Reactor temperature [°C]</strong></td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td><strong>Biomass feed rate [kg/h]</strong></td>
<td>0.2</td>
<td>3.5</td>
</tr>
<tr>
<td><strong>Water content [wt.%]</strong></td>
<td>34.7</td>
<td>17.8</td>
</tr>
</tbody>
</table>
Accelerated aging and analysis of bio-oils

Bio-oil #1 (UGent)
Accelerated aging at 80 °C
Aging time: 4h up to 168h
Aged bio-oil samples
Analysis
KF water content
Micro-carbon residue
Kinematic viscosity
Carbonyl titration

Bio-oil #2 (BTG)
Accelerated aging at 80 °C
Aging time: 4h up to 24h
Aged bio-oil samples

Karl Fischer titrator
Micro-carbon residue tester
Introduction
Materials and methods
Results
Conclusions
Micro carbon residue test results

Micro-carbon residue (wt%, wet basis) results of bio-oil #1 (UGent) over time following accelerated aging at 80°C.
Viscosity test results over aging time

Bio-oil #1 (UGent)

Bio-oil #2 (BTG)
Micro carbon residue test results

- Two bio-oils initially had similar MCR value, despite different initial water contents.
- Bio-oil #2 (BTG) had a smaller increase in MCR compared to bio-oil #1 (UGent).
- Bio-oil #2 (BTG) had a better correlation with aging period.

MCR values [wt.%] (dry basis) of Bio-oil #1 (UGent) and Bio-oil #2 (BTG) during accelerated aging.
A good correlation was found in change in viscosity vs change in MCR value for bio-oil #2 (BTG).

MCR increase based method can be used as an alternative assessment method.
Carbonyl titration test results and correlation with MCR

Carbonyl content for bio-oil #2 (BTG) over accelerated aging time

Correlation between change in carbonyl content and change in MCR (%) for bio-oil #2 (BTG)

Carbonyl content (mmol/g bio-oil)

Aging time (hours)

Change in carbonyl content (%)

Change in MCR (%)
Introduction
Materials and methods
Results
Conclusions
Conclusions

– Proposed MCR based evaluation of stability proved to be successful (especially for bio-oils having high water content).
– Bio-oil #1 (UGent) showed a higher rate of increase in MCR values compared to bio-oil #2 (BTG) suggesting that high water content may facilitate aging reactions.
– Assessing MCR values of bio-oils is useful for further upgrading of bio-oil since it shows the coke forming tendency.