Catalyst deactivation in catalytic pyrolysis of biomass

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**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.
Catalytic fast pyrolysis of biomass for fuels/chemicals

- Gas
  - Olefins ($C_2H_4$, $C_3H_6$)
- Bio-oil
  - Refinery co-feedstock
  - Platform chemicals (BTX) - Low C yields, High CO$_x$, High Coke
- Char and coke

Objective: Investigate the effects of catalyst deactivation (by coke formation) on CFP process
Catalytic fast pyrolysis of biomass: literature data with HZSM-5

2015, Mukarakate et al., Green Chemistry, (16), 1444-1461
Processing options for catalytic fast pyrolysis of biomass

### Pros

**Process heat carrier**

**Immediate vapor/catalyst contact**

**Catalyst attrition**

**Process heat carrier (reduced thermal conductivity)**

### Cons

**Biomass ash**

**Temperature inflexibility**

**Catalyst attrition**

### In-situ CFP

### Ex-situ CFP

**Reduced interaction with biomass ash**

**Flexibility in catalytic process conditions**

**Reactor cost**

**Secondary reactions**
Experimental set-up and process conditions

### Operational conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{pyrolysis reactor}}$ ($^\circ$C)</td>
<td>500</td>
</tr>
<tr>
<td>$T_{\text{catalytic reactor}}$ ($^\circ$C)</td>
<td>500</td>
</tr>
<tr>
<td>Biomass feed rate (g/h)</td>
<td>165 – 195</td>
</tr>
<tr>
<td>Experimental run time (min.)</td>
<td>5 – 180</td>
</tr>
<tr>
<td>$N_2$ flow rate (L/h)</td>
<td>72</td>
</tr>
<tr>
<td>Biomass/catalyst (B/C) (-)</td>
<td>0.4 – 14.6</td>
</tr>
<tr>
<td>WHSV (h$^{-1}$)</td>
<td>4.1 – 4.8</td>
</tr>
</tbody>
</table>

### Catalyst (HZSM-5) properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$:Al$_2$O$_3$ ratio</td>
<td>23</td>
</tr>
<tr>
<td>BET surface area [m$^2$/g]</td>
<td>307</td>
</tr>
<tr>
<td>V$_{\text{micro}}$ [cm$^3$/g]</td>
<td>0.08</td>
</tr>
<tr>
<td>V$_{\text{total}}$ [cm$^3$/g]</td>
<td>0.44</td>
</tr>
<tr>
<td>Total acidity [mmol NH$_3$/g catalyst]</td>
<td>0.92</td>
</tr>
<tr>
<td>at 230°C</td>
<td>0.65</td>
</tr>
<tr>
<td>at 432°C</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Extrudates 1.0 – 2.0 mm
Experimental plan

Ex-situ catalytic fast pyrolysis

SET I
Online (during process)
- Catalytic bio-oil collection at various time-on-stream intervals
  - GC/MS analysis
  - Elemental analysis
  - KF water content

SET II
Offline (after the process)
- Spent catalyst collection at various time-on-stream
  - Elemental analysis
  - BET, acidity, pore volume
  - Coke content
SET I - Change in product yields over selected time intervals

- Decreasing gas and coke yields
- Increasing organics yield

Yields (wt.%, on feed basis)

Organics | Water | Gas | Char | Coke

<table>
<thead>
<tr>
<th>Time-on-stream intervals (minutes)</th>
<th>0 - 40</th>
<th>40 - 80</th>
<th>80 - 120</th>
<th>120 - 160</th>
<th>160 - 200</th>
<th>NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organics (wt.%)</td>
<td>4.5</td>
<td>2.5</td>
<td>1.3</td>
<td>16.0</td>
<td>16.0</td>
<td>16.0</td>
</tr>
<tr>
<td>Water (wt.%)</td>
<td>16.0</td>
<td>29.1</td>
<td>25.6</td>
<td>24.7</td>
<td>24.2</td>
<td>21.7</td>
</tr>
<tr>
<td>Gas (wt.%)</td>
<td>32.5</td>
<td>22.4</td>
<td>25.2</td>
<td>30.5</td>
<td>25.8</td>
<td>17.7</td>
</tr>
<tr>
<td>Char (wt.%)</td>
<td>22.8</td>
<td>21.2</td>
<td>22.1</td>
<td>28.0</td>
<td>25.2</td>
<td>43.2</td>
</tr>
<tr>
<td>Coke (wt.%)</td>
<td>9.0</td>
<td>2.7</td>
<td>5.5</td>
<td>8.3</td>
<td>11.0</td>
<td>NC</td>
</tr>
</tbody>
</table>

Biomass/catalyst (-)

- 0 - 2.7
- 2.7 - 5.5
- 5.5 - 8.3
- 8.3 - 11.0
- 11.0 - 13.8
SET I - Appearance of catalytic bio-oils and phase distribution

Increasing time-on-stream (minutes)
SET I – GC/MS analysis results

- Aromatics yield decrease
- PAHs peak at B/C ratio of 2.7
- Total response decrease
SET I – Oxygen reduction vs. carbon yield

Oxygen reduction
\[
\xi_0 = (1 - \frac{O_{oil}}{O_{feed}}) \times 100\%
\]

Carbon yield
\[
\eta_c = \left( \frac{\text{moles}_{Coil}}{\text{moles}_{Cfeed}} \right) \times 100\%
\]
Experimental plan

Ex-situ catalytic fast pyrolysis

SET I
Online (during process)

Catalytic bio-oil collection at various time-on-stream intervals
- GC/MS analysis
- Elemental analysis
- KF water content

SET II
Offline (after the process)

Spent catalyst collection at various time-on-stream
- Elemental analysis
- BET, acidity, pore volume
- Coke content
SET II – Product yields

Time on stream (minutes)

<table>
<thead>
<tr>
<th>Time on Stream (minutes)</th>
<th>Product Yields (wt.%, on feed basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 5</td>
<td>9.3 (Organics 16, Water 33.4, Gas 36.0, Char 16, Coke 16)</td>
</tr>
<tr>
<td>0 - 10</td>
<td>8.6 (Organics 16, Water 36.5, Gas 31.1, Char 16, Coke 16)</td>
</tr>
<tr>
<td>0 - 15</td>
<td>5.9 (Organics 16, Water 38.3, Gas 24.2, Char 16, Coke 16)</td>
</tr>
<tr>
<td>0 - 20</td>
<td>5.4 (Organics 16, Water 29.4, Gas 27.6, Char 16, Coke 16)</td>
</tr>
<tr>
<td>0 - 40</td>
<td>4.0 (Organics 16, Water 28.5, Gas 24.3, Char 16, Coke 16)</td>
</tr>
<tr>
<td>0 - 60</td>
<td>3.4 (Organics 16, Water 31.9, Gas 23.6, Char 16, Coke 16)</td>
</tr>
<tr>
<td>0 - 120</td>
<td>2.0 (Organics 16, Water 26.6, Gas 25.1, Char 16, Coke 16)</td>
</tr>
<tr>
<td>0 - 180</td>
<td>1.5 (Organics 16, Water 25.9, Gas 30.9, Char 16, Coke 16)</td>
</tr>
<tr>
<td>NC (0 - 120 min.)</td>
<td>16 (Organics 17.7, Water 21.7, Gas 43.2, Char 16, Coke 16)</td>
</tr>
</tbody>
</table>
SET II – Deoxygenation pathways

- Deoxygenation pathway is dehydration alongside decarbonylation
- Total oxygen rejection converges to NC case
SET II – Coke yields and composition

Coke yields (wt.%) as a function of time on stream (minutes):
- Coke yield (wt.%) feed basis
- Coke yield (wt.%) vapor basis

Coke - H/C atomic ratio

Soft coke region*
Hard coke region*

*2001, Bartholomew, App. Cat. A (212) 17-60
SET II – Spent catalyst characteristics

- BET Surface area (m²/g)
- TPD-NH₃ (µmol/g)
- Pore volume (ml/g)

R² values:
- BET Surface area: 0.99
- TPD-NH₃: 0.89
- Pore volume: 0.98
SET II – Spent catalyst characteristics

![Graph showing the relationship between coke-on-catalyst (wt.%) and BET Surface area, TPD-NH₃, and Pore volume](image)

- **BET Surface area (m²/g)**
- **TPD-NH₃ (µmol/g)**
- **Pore volume (ml/g)**

- **R² = 1.00**
- **R² = 0.88**
- **R² = 0.99**

Coke-on-catalyst (wt.%) increases with increasing time on-stream.
SET II – Exothermic nature of CFP reactions

- Temperature increase indicates exothermic reactions.
- And it correlates with coke formation.

![Graph showing temperature vs. time-on-stream and coke content](image-url)

- **Temperature (°C)**
- **Coke (wt.%)**
Conclusions

- Conventional HZSM-5 based catalyst started to deactivate at around biomass/catalyst ratio of 2.7 (in agreement with literature data).
- Catalyst deactivation was observed by change in product yields (converging to NC case), decrease in deoxygenated products (BTX, PAHs).
- **Hard coke (aromatic in nature and harder to remove)** becomes dominant as the catalyst deactivates.
- **Coke formation** correlates well with decreases in BET surface area, pore volume and acidity indicating it is the primary form of catalyst deactivation.
- Temperature increase over the catalyst bed indicated the **exothermic nature** of the CFP process.
Questions?

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