Experimental Black Liquor Devolatilization Measurements

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Devolatilization Studies

- Devolatilization studied in a laminar entrained-flow reactor (LEFR)
  - Fast heating rates ($10^3 – 10^4$ °C/s)
  - Rapid cooling
  - Negligible temperature gradients within particles
- Devolatilization of three liquors to be studied at Chalmers in a LEFR
- Prior data from a LEFR for one liquor from IPST
Laminar Entrained-Flow Reactor

Devolatilization Data

- Frederick et al. 1999
  - 400-600°C
  - Kobayashi type devolatilization model for fixed C, N, and S
- Iisa and Jing, 2001
  - 700-1000°C
  - Data for C, H, N, S loss, evolution of gaseous C and S species
High Temperature Data from Iisa and Jing

Fixed Carbon Remaining in Char

- Model
- 700°C
- 800°C
- 900°C
- 1000°C

Time, s

Fixed Carbon in Char

0% 20% 40% 60% 80% 100%

0 0.1 0.2 0.3 0.4 0.5
Kobayashi Model

\[-\frac{dC}{dt} = k_1C\]
\[-\frac{dC}{dt} = k_2C\]

Fuel (C)

Volatile 1 (V₁) + Char 1 (S₁)

\[dV₁/dt = \alpha₁ k₁C\]
\[dS₁/dt = (1 - \alpha₁) k₁C\]

Volatile 2 (V₂) + Char 2 (S₂)

\[dV₂/dt = \alpha₂ k₂C\]
\[dS₂/dt = (1 - \alpha₂) k₂C\]

Constants for Kobayashi Model

<table>
<thead>
<tr>
<th></th>
<th>Fixed C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha₁)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(A₁, \ s^{-1})</td>
<td>6.3</td>
<td>0.74</td>
<td>4.8</td>
</tr>
<tr>
<td>(E_{a₁}, \ kJ/mol)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\alpha₁)</td>
<td>1.0</td>
<td>0.8</td>
<td>0.88</td>
</tr>
<tr>
<td>(A₁, \ s^{-1})</td>
<td>4.0x10²</td>
<td>3.3x10⁴</td>
<td>5.3x10²</td>
</tr>
<tr>
<td>(E_{a₁}, \ kJ/mol)</td>
<td>33</td>
<td>70</td>
<td>32</td>
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</table>
Comparison of Kobayashi Models from Low and High Temperature Data

Fixed Carbon

Fit of Low Temperature Model to Both Data
Fit of High Temperature Model to Both Data

Fit of Combined Model to Both Data
Constants for Kobayashi Model

<table>
<thead>
<tr>
<th>Data included</th>
<th>Low T</th>
<th>High T</th>
<th>Low T + High T</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.10</td>
<td>0</td>
<td>0.17</td>
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<tr>
<td>$A_1$, s$^{-1}$</td>
<td>1.0</td>
<td>6.3</td>
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<td>$E_{a1}$, kJ/mol</td>
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<td>0</td>
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<td>$\alpha_2$</td>
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<td>0.83</td>
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<td>$A_2$, s$^{-1}$</td>
<td>0.67</td>
<td>4.0x10$^2$</td>
<td>1.2x10$^5$</td>
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<tr>
<td>$E_{a2}$, kJ/mol</td>
<td>2.3</td>
<td>33</td>
<td>82</td>
</tr>
</tbody>
</table>

Fits for N
Fit of Low Temperature Model to Both Data

Fit of High Temperature Model to Both Data
Fit of Combined Model to Both Data

Parameters for Kobayashi Model: Nitrogen

<table>
<thead>
<tr>
<th>Data included</th>
<th>Low T</th>
<th>High T</th>
<th>Low T + High T</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.43</td>
<td>0</td>
<td>0.17</td>
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<tr>
<td>$A_1$, s$^{-1}$</td>
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<td>4.8</td>
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<tr>
<td>$E_{a1}$, kJ/mol</td>
<td>10</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>-</td>
<td>0.88</td>
<td>1.0</td>
</tr>
<tr>
<td>$A_2$, s$^{-1}$</td>
<td>-</td>
<td>5.3x10$^2$</td>
<td>1.2 x10$^3$</td>
</tr>
<tr>
<td>$E_{a2}$, kJ/mol</td>
<td>-</td>
<td>32</td>
<td>47</td>
</tr>
</tbody>
</table>
Conclusions

• Laminar Entrained Flow Reactors can be used to obtain devolatilization data at high heating rates
  – Total mass (char yield)
  – C, H, N, S, Na, K, Cl
• It is possible to extract kinetic constants from the data

Conclusions

• Data required in a wide range of temperatures to obtain useful predictions
  – Data obtained at low temperatures only fails to predict behavior at high temperatures
  – Data obtained at high temperatures only does not adequately predict slower devolatilization rates or variation in final char yields at lower temperatures