Experimental Black Liquor Devolatilization Measurements

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Devolatilization Studies

- Devolatilization studied in a laminar entrained-flow reactor (LEFR)
  - Fast heating rates ($10^3 - 10^4 \, ^\circ C/s$)
  - 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

Three-Zone Furnace

Dry Solids Primary Gas

Secondary Gas

Cooling Water

Quench Gas

Cyclone

Collector

Gas for Analysis

Fine Particle Filter
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 Lisa 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%
Hydrogen Remaining in Char

Model

700°C

800°C

900°C

1000°C

Hydrogen in Char

Time, s
Nitrogen Remaining in Char

![Graph showing nitrogen remaining in char at different temperatures (700°C, 800°C, 900°C, 1000°C). The x-axis represents time in seconds (0-0.6), and the y-axis represents nitrogen in char (%). The graph includes model predictions and experimental data points.]
Kobayashi Model

Fuel (C)

-Volatile 1 (V₁) + Char 1 (S₁)
\[ \frac{dV_1}{dt} = \alpha_1 k_1 C \]
\[ \frac{dS_1}{dt} = (1-\alpha_1) k_1 C \]

-Volatile 2 (V₂) + Char 2 (S₂)
\[ \frac{dV_2}{dt} = \alpha_2 k_2 C \]
\[ \frac{dS_2}{dt} = (1-\alpha_2) k_2 C \]
## Constants for Kobayashi Model

<table>
<thead>
<tr>
<th></th>
<th>Fixed C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$A_1$, 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>$\alpha_1$</td>
<td>1.0</td>
<td>0.8</td>
<td>0.88</td>
</tr>
<tr>
<td>$A_1$, s$^{-1}$</td>
<td>$4.0 \times 10^2$</td>
<td>$3.3 \times 10^4$</td>
<td>$5.3 \times 10^2$</td>
</tr>
<tr>
<td>$E_{a1}$, kJ/mol</td>
<td>33</td>
<td>70</td>
<td>32</td>
</tr>
</tbody>
</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>
</tr>
<tr>
<td>$A_1$, s$^{-1}$</td>
<td>1.0</td>
<td>6.3</td>
<td>147</td>
</tr>
<tr>
<td>$E_{a1}$, kJ/mol</td>
<td>0</td>
<td>0</td>
<td>23</td>
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<tr>
<td>$\alpha_2$</td>
<td>0.54</td>
<td>1.0</td>
<td>0.83</td>
</tr>
<tr>
<td>$A_2$, s$^{-1}$</td>
<td>0.67</td>
<td>4.0x10$^2$</td>
<td>1.2x10$^5$</td>
</tr>
<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

[Graph showing the fit of low temperature model to data across different temperatures (400°C to 1000°C) and time (0 to 2 seconds), with nitrogen content in char on the y-axis and time on the x-axis. The graph includes various lines and markers representing different temperatures.]
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>
<td>5.5</td>
<td>4.8</td>
<td>75</td>
</tr>
<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>5.3 x 10$^2$</td>
<td>1.2 x 10$^3$</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