Kraft Black Liquor Gasification Kinetics

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# KBL Chars Studied

<table>
<thead>
<tr>
<th>Moisture content(%)</th>
<th>Pine</th>
<th></th>
<th>Birch</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kraft</td>
<td>Soda-AQ</td>
<td>Kraft</td>
<td>Soda-AQ</td>
</tr>
<tr>
<td>Concentrated</td>
<td>30.6</td>
<td>23.7</td>
<td>26.7</td>
<td>28.3</td>
</tr>
<tr>
<td>“dry”</td>
<td>6.8</td>
<td>4.4</td>
<td>11.3</td>
<td>6.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pyrolysis rate</th>
<th>Heating rate ($^\circ$C)</th>
<th>Pyrolysis $T_{\text{final}}$ ($^\circ$C)</th>
<th>Time at $T_{\text{final}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow</td>
<td>0.03</td>
<td>700</td>
<td>120</td>
</tr>
<tr>
<td>Medium</td>
<td>210</td>
<td>750</td>
<td>6</td>
</tr>
<tr>
<td>Fast</td>
<td>715</td>
<td>750</td>
<td>9</td>
</tr>
</tbody>
</table>
Relationship between Char Specific Volume (Swelling) and BET Surface Area

- Rough correlation between swelling and BET
- Fast pyrolysis leads to more swelling (except for birch)
Effect of Pyrolysis Rate on Gasification Rate, \(-r = -\frac{1}{C_t} \frac{dC_t}{dt} (1/\text{min})\)

- \(r\) is constant for slow pyrolysis char; first order in carbon
- \(r\) at \(X=0.5\) is twice as high as at \(X = 0.0\); zero order in carbon
Effect of Liquor Type on Gasification Rate of Slow Pyrolysis Chars

- All slow pyrolysis chars show first order in carbon
- Reaction order: Pine kraft > Birch Kraft > Pine Soda-AQ > Birch Soda-AQ
Gasification Rate and Specific Volume for Fast Pyrolysis Char

No correlation between rate and degree of swelling
Gasification Rate and Specific Volume for Slow Pyrolysis Char

Weak correlation between rate and degree of swelling
Effect of BET Surface on $-r_{25\%}$ for Slow Pyrolysis chars

Slow pyrolysis chars do not correlate well with Na/C molar ratio, however rate increases with size of BET surface. This is inconsistent with the reaction being first order in carbon.
Effect of Na/C$_{\text{org}}$ Molar Ratio on $-r_{25\%}$ for Fast Pyrolysis chars

Gasification rate of fast pyrolysis chars proportional to Na/C ratio up to Na/C $\sim 1.0$, and but independent of Na/C ratio when Na/C $> 1.0$

This is consistent with the rate being first order in sodium content and zero order in carbon for Na/C smaller than 1.0

Gasification Conditions
- $T=700^\circ$C
- $[H_2O]=15\%$
- $[H_2]=2.0\%$
- 1 atm total pressure
Summary of Effect of Pyrolysis Rate and Liquor Type

- **Slow Pyrolysis Char Reactivity**
  - First order in carbon
  - Increases with BET surface
  - Pine kraft > birch kraft > pine-soda-AQ > birch soda-AQ

- **Fast Pyrolysis Char Reactivity**
  - Zero order in carbon
  - Not affected by degree of swelling
  - First order in sodium up to Na/C = 1.0
  - Birch kraft > pine kraft > soda-AQ
Explanation for Difference in Reactivity Behavior

- **Slow Pyrolysis Char Reactivity**
  Poor dispersion of Na catalyst so that reactivity is determined by availability of carbon surface

- **Fast Pyrolysis Char Reactivity**
  Good dispersion of Na catalyst so that reactivity is determined by number of Na active sites

- **Kraft Chars more reactive than Soda-AQ**
  \[ T_{\text{melt}} \text{ of } (\text{Na}_2\text{S} + \text{Na}_2\text{CO}_3) < T_{\text{m}} \text{ of } \text{Na}_2\text{CO}_3 \]
Mechanism of Carbon Gasification by CO$_2$

\[
\begin{align*}
M_2CO_3 + C & \rightarrow (-CO_2M) + (-COM) \\
(-COM) + CO_2 & \xrightleftharpoons[\frac{k_2}{k_2}]{k_2} (-CO_2M) + CO \\
(-CO_2M) + C & \rightarrow^k (-COM) + CO \\
C + CO_2 & \leftrightarrow 2CO
\end{align*}
\]

(-COM) is phenolic alkali metal surface oxide group

(-CO$_2$M) is carboxylic alkali metal surface oxide group

• KBL gasification rate is O(10,000) times that of graphite
Kinetics of Carbon Gasification by CO$_2$

When $k_3$ is much smaller than $k_{-2}[CO_2]$, then

$$-r = -\frac{1}{C_t} \frac{dC_t}{dt} = \frac{k_3[CO_2]}{[CO_2] + \frac{k_{-2}}{k_2}[CO]} \text{ (s}^{-1}\text{)}$$
Kinetics of Carbon Gasification by CO₂

By combining data from Li (1990) and van Heiningen et al (1994):

\[-r_c = \frac{7 \times 10^{10} K_1[CO_2]e^{-30,070/T(K)}}{[CO_2] + K_2[CO]} \left( \frac{\text{moles} \cdot \text{carbon}}{m^3 \cdot s} \right)\]

with \(K_2 = 3.4\), and

- For fast pyrolysis char
  \(K_1 = [\text{Na}]\) (moles sodium/m³), when \([C] \geq [\text{Na}]\)
  \(K_1 = [\text{C}]\) (moles carbon/m³), when \([C] < [\text{Na}]\)

- For slow pyrolysis char
  \(K_1 = [\text{C}]\) (moles carbon/m³)
Mechanism and Kinetics of Carbon Gasification by H₂O

\[
(-\text{COM}) + \text{H}_2\text{O} \overset{k_4}{\underset{k_{-4}}{\leftrightarrow}} (-\text{CO}_2\text{M}) + \text{H}_2 \\
(-\text{CO}_2\text{M}) + \text{C} \rightarrow (-\text{COM}) + \text{CO} \\
\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2
\]

\[
-r_c = \frac{3 \times 10^9 K_3 [\text{H}_2\text{O}] e^{-25,200/T(K)}}{[\text{H}_2\text{O}] + K_4 [\text{H}_2]} \left( \frac{\text{moles} \cdot \text{carbon}}{m^3 \text{s}} \right)
\]

with \( K_4 = 1.42 \), and

- For fast pyrolysis char: \( K_3 = [\text{Na}] \) (moles sodium/m³), when \([\text{C}] \geq [\text{Na}]\)
- \( K_3 = [\text{C}] \) (moles carbon/m³), when \([\text{C}] < [\text{Na}]\)
- For slow pyrolysis char: \( K_3 = [\text{C}] \) (moles carbon/m³)
Conclusion

• Black liquor gasification is extremely fast

• Kinetics of slow pyrolysis chars are:
  – First order in carbon
  – Increasing with BET surface

• Kinetics of fast pyrolysis chars are:
  – Zero order in carbon
  – First order in sodium up to Na/C = 1.0

• Effect of elevated pressure needs further study