Thermochemical modeling of the inorganic reactions in pressurized black liquor gasification

Daniel Lindberg, Rainer Backman
PCG-Combustion and materials Chemistry
Åbo Akademi University

Colloquium on Black Liquor Combustion and Gasification
May 13-16, 2003
Park City, Utah
Pressurized black liquor gasification

– Possible compliment to the Kraft Recovery Boiler

– Different concepts
  • High / low temperature gasification
  • Fluidized bed / Entrained flow
Background

– Melting behavior of the inorganics and the behavior of the elements relevant for the chemical recovery are dependent on:

  • Black liquor composition
  • Process parameters

– Thermochemical modeling is a good stand-alone tool or submodel for predicting the chemistry at varying physical and chemical conditions
Objective

– **Apply** thermodynamical equilibrium modeling to **predict** the inorganic chemistry in **pressurized** black liquor gasification

  • Melting behavior of the inorganics
    – Slagging & Fouling
    – Corrosion
    – Bed agglomeration

  • Recovery of pulping chemicals
    – Sulfur in a gaseous or condensed phase
    – Volatilization of Sodium
Thermodynamical equilibrium modeling in combustion and gasification systems

Result:
Gaseous Products (composition and amount)

Composition input
- Fuel
  - Organic part
  - Ash
  - $\text{H}_2\text{O}$
- Air

Equilibrium Reactor

\[ v = \frac{NRT}{P} \]

System input
- Thermodynamic data for all species ($H, S, Cp$ or $G = f(T)$)
- Solution parameters

Result:
Condensed Products (composition and amount)
Solids, Melts

Composition input: Fuel, Air
System input: Thermodynamic data, Solution parameters
Result: Gaseous Products, Condensed Products

Software tools:
FactSage, ChemSage, ChemSheet, ChemApp
# Thermochemical modeling of pressurized black liquor gasification

Black liquor composition (Wt-% DS)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt-% DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>37</td>
</tr>
<tr>
<td>H</td>
<td>4</td>
</tr>
<tr>
<td>O</td>
<td>35</td>
</tr>
<tr>
<td>Na</td>
<td>17</td>
</tr>
<tr>
<td>S</td>
<td>3.8 - 7.4 (Sulfidity = 0.3 or 0.6)</td>
</tr>
<tr>
<td>K</td>
<td>1.5</td>
</tr>
<tr>
<td>Cl</td>
<td>0.2 - 1.1</td>
</tr>
</tbody>
</table>

Temperature: 400-1600 °C  
Pressure: 1-100 bar  
Air/Fuel ratio: 0 - 1
Melting range of inorganics at gasification conditions
AR<0.6, varying black liquor composition

<table>
<thead>
<tr>
<th>Pressure [bar]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>600</td>
</tr>
<tr>
<td>600</td>
<td>650</td>
</tr>
<tr>
<td>650</td>
<td>700</td>
</tr>
<tr>
<td>700</td>
<td>750</td>
</tr>
<tr>
<td>750</td>
<td>800</td>
</tr>
<tr>
<td>800</td>
<td>850</td>
</tr>
</tbody>
</table>

- **Only molten**
- **Melt + solid mixture**
- **Only solid**

Melting range
Melting properties of the inorganic salts

$P = 10\text{ bar, } \lambda = 0.3$

$T_{70} = \text{flow temperature}$

$T_{15} = \text{sticky temperature}$
Melting properties of the inorganic salts

$P = 10$ bar, $\lambda = 0.3$

$T_{70} =$ flow temperature

$T_{15} =$ sticky temperature

Low S, High Cl

Low S, Low Cl
Melting properties of the inorganic salts

$P = 10$ bar, $\lambda = 0.3$

$T_{70} =$ flow temperature

$T_{15} =$ sticky temperature

Low S, Low Cl

Low S, High Cl
Melt fraction at $T=700 \, ^\circ C$, $P=10$ bar, $AR=0.3$
S distribution

P=10 bar, λ=0.3

Mol-% (cumulative)

Temperature [°C]

(Na,K)$_2$S (l)

COS (g)

H$_2$S (g)

(Na,K)$_2$S (melt)
S distribution

T=1000 °C, \( \lambda = 0.3 \)
S distribution

T=1000 °C, P=10 bar

Air/Fuel ratio

Mol-% (cumulative)

- H₂S (g)
- COS (g)
- SO₂
- (Na,K)₂S (l)
- (Na,K)₂SO₄ (l)
Na distribution
T = 1200 °C, λ=0.0

- Gaseous Na
- NaOH (l)
- NaCl (s,l)
- Na₂S (l)
- Na₂CO₃ (l)
Na distribution

T=1200 °C, P=10 bar

Mol-% (cumulative)

Air/Fuel ratio

Na (g)
NaOH (l)
NaCl (l)
Na₂CO₃ (s,l)
Na₂S (l)
Na₂SO₄ (l)
Conclusions (I)
Melting properties

• Melting range: 570-590 °C → 750-850 °C
• High Cl content in black liquor
  → Sticky temperature significantly lowered
    (up to 100 °C)
• At low-T gasification conditions:
  – Melt fraction highly variable → agglomeration of
    bed material is possible
Conclusions (II)
Behavior of Na and S

• In low-T gasification
  – Most sulfur as gaseous \(H_2S\)

• In high-T gasification
  – Sulfur as gaseous \(H_2S\) or in melt
    • High T
    • Low P
    • Low \(\lambda\)  
      Sulfur in melt
Conclusions (II)
Behavior of Na and S

• In low-T gasification
  – Sodium in solid salts or salt melt

• In high-T gasification
  – Sodium mainly in melt
    • High T
    • Low P
      Sodium volatilized
    • Low λ