Introduction to Kraft process

- Black liquor
  and
The black liquor recovery boiler
• Kraft chemical pulping

Wood + Pulping chemicals (Na$_2$S, NaOH)

155°C
900 kPa

Lignin etc.

Fibers

Black liquor
A 1000 t/d Kraft pulp mill produces 1500 t/d BL d.s.
## As-Fired Black Liquor Composition
(750 liquor samples; All Wood Species)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Typical</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids content, %</td>
<td>72</td>
<td>65 – 85</td>
</tr>
<tr>
<td>HHV, MJ/kg</td>
<td>13.9</td>
<td>12.5 – 15.5</td>
</tr>
<tr>
<td>C, wt% d.s.</td>
<td>33.9</td>
<td>30 – 40</td>
</tr>
<tr>
<td>H</td>
<td>3.4</td>
<td>3.2 – 4.0</td>
</tr>
<tr>
<td>O</td>
<td>35.8</td>
<td>34 – 38</td>
</tr>
<tr>
<td>Na</td>
<td>19.6</td>
<td>17 – 22</td>
</tr>
<tr>
<td>S</td>
<td>4.6</td>
<td>3.6 – 5.6</td>
</tr>
<tr>
<td>K</td>
<td>2.0</td>
<td>1 – 3</td>
</tr>
<tr>
<td>Cl</td>
<td>0.5</td>
<td>0.1 – 4</td>
</tr>
</tbody>
</table>
Black liquor recovery boiler

- Recovery of chemicals and heat

Recovered chemicals

Wood
- Chemicals
- Water

Chemical pulping

Fibers

Recovery processes
- Recovery Boiler
- Black liquor is burned

Black liquor
- Organic matter
- Spent chemicals
- Water

Heat
Black liquor droplet burning

800 °C, 19% O₂
Stages of combustion

Drying

Removal of water and combustion of organic matter

Devolatilization

Inorganics → pulping chemicals

Char combustion

Smelt bead
Chemicals recovery in the Kraft process

- **Digester**
  - Wood chips
  - Pulp

- **Black liquor** (15% DS)
  - \( Na_2CO_3 \)
  - \( Na_2SO_4 \)

- **Evaporators**

- **Recovery boiler**

- **Steam turbine**
  - (Power)
  - Process steam

- **Steam**

- **Flue gas**

- **Causticizing**
  - \( NaOH \)
  - \( Na_2S \)

- **Dissolver**
  - \( Na_2CO_3 \)
  - \( Na_2S \)

- **Green liquor**

- **Lime kiln**
  - \( CaCO_3 \)

- **Lime**
  - \( CaO \)

- **White liquor**

- **Water**

Chemical reactions:

- \( CaO + H_2O \rightarrow Ca(OH)_2 \)
- \( Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3 \)

*(K Whitty)*
Black liquor recovery boiler
First Tomlinson recovery boiler (1937)

15 m
Black liquor combustion in the recovery boiler

Recovery of
1) Heat
2) Chemicals

By
1) Oxidizing organic matter
2) Reducing $\text{Na}_2\text{SO}_4$ to $\text{Na}_2\text{S}$
Black liquor combustion in the recovery boiler

Power & process steam → Steam

Superheaters

Flue gas

Air

Black liquor

Smelt
Black liquor combustion in the recovery boiler

- Black liquor spray
- In-flight combustion

- Char bed
- Material input by droplets
- Char bed burning
Black liquor combustion in the recovery boiler

Black liquor spraying
Nozzle Types

- Swirlcone Nozzle
- V-Type Nozzle
- Splash Plate Nozzle
- Beer Can Nozzle

Typical Nozzle Gun Assembly

(Rick Wessel)
Splash Plate Nozzle Geometry

Looking down on a splash plate nozzle

35° plate angle

45° plate angle

(Rick Wessel)
Three Temperature Regimes

Non-Flashig

Transitional

Flashing

$\Delta T_e = -4.1 \, ^\circ C$

$\Delta T_e = 4.7 \, ^\circ C$

$\Delta T_e = 14.8 \, ^\circ C$

Solids = 69%, EBP = 115°C

Excess Temperature, $\Delta T_e = T - T_{EBP}$

(Rick Wessel)
Black Liquor Flashing

Non-flashing

Flashing

Higher nozzle velocity due to expansion of steam bubbles

(Rick Wessel)
Effect of Temperature on Drop Size

\[ D_{\text{median}} \propto \frac{1}{T^{0.14}} \]

Note: liquor mass flow rate, solids, and nozzle diameter are fixed

(Rick Wessel)
Black liquor spraying – droplet size distribution

Particle Size Distribution of Black Liquor Sprays with A High Solids Content in Recovery Boilers
A. Kankkunen and P. Muikkulainen

$T_{excess}$

18°C

17°C

14°C
Particle Size Distribution of Black Liquor Sprays with A High Solids Content in Recovery Boilers
A. Kankkunen and P. Muikulainen

Mass flow: 4.3 kg/s, 5.3 kg/s, 6.1 kg/s

Temperature: 18°C, 17°C, 14°C

Volume fraction of particles
Black liquor spraying – droplet size distribution

Particle Size Distribution of Black Liquor Sprays with A High Solids Content in Recovery Boilers
A. Kankkunen and P. Muikulainen

Excess Temperature

18°C

17°C

14°C

Mass flow

4.3 kg/s

5.3 kg/s

6.1 kg/s
Droplets should deliver char carbon to bed

**Goal:**  \[ \text{Na}_2\text{SO}_4(\text{l}) + 4\text{C}(\text{s}) \rightarrow \text{Na}_2\text{S}(\text{l}) + 4\text{CO}(\text{g}) \]

**Avoid:**  \[ \text{Na}_2\text{S}(\text{l}) + 2\text{O}_2(\text{g}) \rightarrow \text{Na}_2\text{SO}_4(\text{l}) \]

Avoid too wet droplets to bed
- Bed temperature

(Honghi Tran)
Droplet burning
Drying  Pyrolysis  Char combustion  Smelt bead
Effect of droplet size

10 mm

Drying
Effect of droplet size

6 mm

Drying

Pyrolysis

Char combustion
Effect of droplet size

2 mm
Effect of droplet size

0.5 mm
Effect of swelling

6 mm droplet

No swelling

3.6 x
Effect of swelling

2 mm droplet

No swelling

3.6 x
Fate of Droplets in a Recovery Boiler

1. **Entrained**
   - too small and/or too high swelling properties
   - \( \text{Na}_2\text{S} \rightarrow \text{Na}_2\text{SO}_4 \)
   - “carry over” deposits

2. **Reach bed as smelt**
   - still too small and/or too high swelling properties
   - \( \text{Na}_2\text{SO}_4 \) to bed
   - no carbon to bed

3. **Reach bed while burning**
   - optimum size of droplets and/or optimum swelling prop.
   - \( \text{Na}_2\text{S} \) to char bed
   - Carbon to char bed

4. **Reach bed wet**
   - too large droplets and/or too small swelling properties
   - carbon to bed
   - \( \text{Na}_2\text{S} \) produced in bed
   - \( \text{H}_2\text{O} \) to char bed \( \rightarrow \) char bed temperature drops

(Hupa & Frederick)
Char bed
"Härkä"
Matti Reitti, 1975
Char bed
Char bed burning

Char-carbon oxidation

\[ \text{C(s)} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} \]
\[ \text{C(s)} + \text{CO}_2 \rightarrow 2\text{CO} \]
\[ \text{C(s)} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]
\[ \text{C(s)} + \frac{1}{4}\text{Na}_2\text{SO}_4(l) \rightarrow \text{CO} + \frac{1}{4}\text{Na}_2\text{S}(l) \]
Char bed burning

Share of total carbon conversion

35%  17%  13%  35%

Bergroth et al. 2004
Char bed size and shape

- **Goal:** sufficient amount of char for sulfate reduction
  - **Avoid:** too high bed/uncontrolled growth

- **Material balance:** Input vs. Conversion

- **Controlled** via changes in spraying and air delivery
Char bed size and shape

Stable char bed burning important for stable operation of RB
- Example: impact on steam production

Stable bed  Growing bed
Impact of bed operation on steam production

- Process data on liquor spraying

Liquor feed per wall (liters/second)

Impact of bed operation on steam production

Liquor feed per wall (liters/second)

• Process data on liquor spraying

Liquor feed per wall (liters/second)

Impact of bed operation on steam production

Liquor feed per wall (liters/second)

Impact of bed operation on steam production

Liquor feed per wall (liters/second)
Impact of bed operation on steam production

- Lower T → bigger droplets → more carbon to bed

Liquor temperature (°C)

Liquor feed per wall (liters/second)

09.02 10.02 11.02 12.02 13.02

Stable Date Growing
Impact of bed operation on steam production

- Process data on steam production

**Stable Bed**

- 1 Minute
- 1 Hour

**Growing Bed**

Data
Impact of bed operation on steam production
Impact of bed operation on steam production
Fouling

• Carryover
  – Smelt from droplets carried up with flue gases
  – Size mm range

• Fume (dust)
  – Condensed vapors
  – Size μm range

• Cleaning – Soot blowing
Carryover

• Smelt from burning droplets carried up with combustion gases
• Overloaded boilers most susceptible because of large gas flow
• Composition slightly reduced in K and Cl
• If between ~15 and 70% molten ($T_{15}$ and $T_{70}$) it will stick
Fume

- Comprised of alkali salt vapors
- Condense as the gas cools
- Carried to heat transfer surfaces by thermal gradients
- Enriched in K and Cl when compared to BL
- Typically deposit in back end of boiler bank and beginning of economizers
- Problem if sinter significantly before removed by soot blowers
- $T_0$ key variable
Particles From Black Liquor Burning

Entrained BL char

Intermediate Particles

Fume Particles
Fume particles attached on a carry over particle
Composition of Recovery Boiler Fly Ash

**Carry over**
- Burning BL droplets
- Size mm range

**Fume**
- Released Na, K, S and Cl from burning BL droplets
- Evaporated Na, K, S and Cl from smelt bed
- Formed from gas phase
- Size μm range

![Pie chart showing the composition of fly ash](image)
Acidic sulfates - $\text{NaHSO}_4$
- Requires surplus of $\text{SO}_2$ in flue gases
- Partly molten already at $400 - 450^\circ\text{C}$
- Not stable above $450^\circ\text{C}$
- Indications by pH measurements
REATIONS OF S AND Na IN FLUE GASES
(S/Na$_2$ = 0.8, hot lower furnace, low sulphidity)
REATIONS OF S AND Na IN FLUE GASES
(S/Na$_2$ = 1.5, cool lower furnace, high sulphidity)
Types and locations of fouling

- Super Heaters
  - Carry over

- Boiler Bank
  - Sintering of fume

- Economizer & ESP filter
  - Acidic sulfates