Introduction to Kraft process
-
Black liquor
and
The black liquor recovery boiler
Black liquor

- *Kraft chemical pulping*

Wood

Lignin etc.

Fibers

Pulping chemicals

\((\text{Na}_2\text{S}, \text{NaOH})\)

155°C

900 kPa

(Fibers)

Black liquor

(Honghi Tran)
A 1000 t/d Kraft pulp mill produces 1500 t/d BL d.s.

(Honghi Tran)
# 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>

(Honghi Tran)
Black liquor recovery boiler

- Recovery of chemicals and heat

- Wood
- Chemicals
- Water

Recovered chemicals

Chemical pulping

Fibers

Black liquor
- Organic matter
- Spent chemicals
- Water

Recovery processes
- Recovery Boiler
- Black liquor is burned

Heat
Black liquor droplet burning

800 °C, 19% O₂
Black liquor combustion

Stages of combustion

Drying

Removal of water and combustion of organic matter

Devolatilization

Char combustion

Smelt bead

Inorganics → pulping chemicals
Chemicals recovery in the Kraft process

Digester

Wood chips

Pulp

Pulp

Black liquor
15% DS

Na₂CO₃
Na₂SO₄

Evaporators

Steam turbine

(Power)

Process steam

Steam

Recovery boiler

Flue gas

Na₂CO₃
Na₂SO₄

Na₂CO₃
Na₂S

White liquor

CaCO₃

Lime kiln

CaO

CaO + H₂O → Ca(OH)₂
Ca(OH)₂ + Na₂CO₃ → 2NaOH + CaCO₃

Green liquor

Na₂CO₃
Na₂S

Dissolver

Water

(K Whitty)
Black liquor recovery boiler

85 m
First Tomlinson recovery boiler (1937)
Black liquor combustion in the recovery boiler

Recovery of
1) Heat
2) Chemicals

By
1) Oxidizing organic matter
2) Reducing Na$_2$SO$_4$ to Na$_2$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 spraying
Black liquor combustion in the recovery boiler

Black liquor spraying

(Miikkulainen and Kankkunen)
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-Flashing

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

Transitional

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

Flashing

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

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. Muikulainen

$T_{\text{excess}}$

18°C

17°C

14°C
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$T_{\text{excess}}$

18°C

17°C

14°C

Mass flow

4.3 kg/s

5.3 kg/s

6.1 kg/s
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A. Kankkunen and P. Muikulainen

IFRF Combustion Journal
Article Number 200308, December 2003
ISSN 1562-479X

$T_{\text{excess}}$

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: \( \text{Na}_2\text{SO}_4(\text{l}) + 4\text{C(s)} \rightarrow \text{Na}_2\text{S(l)} + 4\text{CO(g)} \)
- Avoid: \( \text{Na}_2\text{S(l)} + 2\text{O}_2(\text{g}) \rightarrow \text{Na}_2\text{SO}_4(\text{l}) \)

Avoid too wet droplets to bed
- Bed temperature

(Honghi Tran)
Droplet burning
Drying

Pyrolysis

Char combustion

Smelt bead

Droplet burning
Effect of droplet size

10 mm
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
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

Video at 64 x normal speed
Char-bed burning

Char-carbon oxidation:

- \( \text{C}(s) + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} \)
- \( \text{C}(s) + \text{CO}_2 \rightarrow 2\text{CO} \)
- \( \text{C}(s) + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \)
- \( \text{C}(s) + \frac{1}{4}\text{Na}_2\text{SO}_4(l) \rightarrow \text{CO} + \frac{1}{4}\text{Na}_2\text{S}(l) \)

(Honghi Tran)
Char bed burning

$\text{O}_2$  $\text{CO}_2$  $\text{H}_2\text{O}$  $\text{SO}_4$

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)

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

- Lower $T \rightarrow$ bigger droplets $\rightarrow$ more carbon to bed

Liquor temperature (°C)

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

- Process data on steam production

**Stable Bed**

- Data
  - 1 Minute
  - 1 Hour

**Growing Bed**

Steam (kg/s)

<table>
<thead>
<tr>
<th>Time</th>
<th>8:00</th>
<th>10:00</th>
<th>12:00</th>
<th>14:00</th>
<th>16:00</th>
<th>18:00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam</td>
<td>115</td>
<td>120</td>
<td>125</td>
<td>130</td>
<td>135</td>
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Impact of bed operation on steam production
Impact of bed operation on steam production

Heat to steam
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 above 15 wt-% molten - 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
Entrained BL char

Particles From Black Liquor Burning

Intermediate Particles

Fume Particles
Fume particles attached on a carry over particle
REATIONS OF S AND Na IN FLUE GASES
(S/Na₂ = 0.8, hot lower furnace, low sulphidity)
REACTIONS OF S AND Na IN FLUE GASES
(S/Na₂ = 1.5, cool lower furnace, high sulphidity)
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
Acidic sulfates - $\text{NaHSO}_4$

- Requires surplus of $\text{SO}_2$ in flue gases
- Partly molten already at 400 - 450$^\circ$C
- Not stable above 450$^\circ$C
- Indications by pH measurements
Types and locations of fouling

- Super Heaters - Carry over
- Boiler Bank & Economizer - Sintering of fume
- Economizer & ESP filter
- Acidic sulfates