The Kraft Recovery Process

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Kraft Pulping Process

- Most important chemical pulping process
- Global kraft pulp production: 130 million metric tons/year (67% of total)
- Advantages
  - High pulp strength
  - Versatility - ability to handle a wide range of wood species
  - Favorable economics - High chemical recovery efficiency (96 - 98%)
Kraft Pulping Process

Black Liquor + White Liquor (NaOH + Na₂S)

155°C
900 kPa

Fibre

Wood

Lignin

Fibre

Black Liquor

A 1000 t/d Kraft Pulp Mill

produces 1500 t/d BL d.s.

8000 ~ 10,000 t/d weak black liquor
Kraft Recovery Process

A Closed Cycle Process with 3 Main Functions:

- Eliminate the waste material (black liquor)
- Recover pulping chemicals (NaOH and Na₂S)
- Generate steam and power
Kraft Recovery Process

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>
Smelt Formation

0.4 kg smelt /kg BL d.s.

C
H
O
Na
S
K
Cl

\( \text{Na}_2\text{CO}_3 \)

\( \text{Na}_2\text{S} \) (Reducing Conditions)

Others:
\( \text{Na}_2\text{SO}_4, \text{NaCl} \)
\( \text{K}_2\text{CO}_3, \text{K}_2\text{S}, \text{K}_2\text{SO}_4, \text{KCl} \)

\( \frac{1}{3} \)
\( \frac{2}{3} \)

\( \text{Smelt Spout} \)

\( \text{Na}_2\text{CO}_3 + \text{Na}_2\text{S} \)
**Makeup Chemicals (Na, S and Ca)**

- **Sodium**
  - 8 to 16 kg/ADt as Na₂O
  - NaOH, Na₂CO₃, Na₂SO₄ (salt cake)
  - Organic Na compounds (acetate, etc.)

- **Sulfur**
  - 1.4 to 4 kg/ADt as S
  - Na₂SO₄, NaSH, H₂SO₄, Na₃H(SO₄)₂, Elemental S
  - S in lime kiln fuels

- **Calcium**
  - 4 to 8 kg/ADt as CaO
  - Purchased lime
  - Lime rock

**Main Sources of NPEs**

(Non Process Elements)

- **Wood**: Si, Al, Cl, K, Mg, Mn, P, Fe, Ni, Cr, etc.
- **Makeup caustic**: Cl
- **Additive**: Si, Mg
- **Makeup lime**: Si, Al, Mg, P, Fe
- **Refractory bricks**: Si, Al
- **Corrosion products**: Fe, Ni, Cr
Types of NPEs

- Form soluble compounds: Cl, K
  - Be with the liquor
  - Accumulate
- Form partially soluble compounds: Si, Al
  - Precipitate under appropriate conditions
- Form insoluble compounds: Most other elements
  - Do not accumulate
  - Be removed from the recovery system with grits, dregs and lime mud/dust

Energy Recovery

1.9 GJ/ADt

1 GJ/t = 0.860 MM Btu/ton
Recovery Boiler Energy Production

- **Steam**
  - Typically 3.5 kg/kg BLds
  - May vary from 2.5 to 3.8 kg/kg BLds

- **Power**
  - A 1000 t/d kraft pulp mill may generate 25 to 35 MW of electricity from black liquor combustion

Technological Advancements

- **Evaporators/concentrators**
  - Falling film, plate-type
  - High solids (75 to 85%)

- **Recovery boilers**
  - High solids firing
  - High steam temperature/pressure
  - High efficiency

- **Recaust and lime kilns**
  - Pressurized filters
  - Lime mud dryer
Recovery Boiler Firing Capacity

Maximum Recovery Boiler Steam Temperature and Pressure

Vakkilainen (2006)
Benefits of High Solids Firing

- Significantly increases steam generation
- Improves combustion stability
- Lower TRS and SO$_2$ emissions
- Less boiler fouling and plugging
- Increase capacity in existing units.

Operating Problems

- Many problems can occur
- They can be:
  - Equipment related
  - Process related
  - Liquor chemistry related
Common Operating Problems

- **Evaporators**
  - Scaling
  - Corrosion
  - High steam consumption
  - Low solids in product liquor

- **Recovery Boilers**
  - Fouling and plugging
  - Tube corrosion and cracking
  - Spout corrosion and cracking
  - Low steam production
  - Poor sootblowing efficiency
  - Poor water circulation
  - Smelt-water emergencies
  - Gaseous/particulate emissions
  - Tube damage by falling deposits
  - Unstable combustion/blackouts
  - “Jelly roll” smelt/smelt run-off
  - Low reduction efficiency
  - High dregs in smelt

- **Lime kiln and Recausticizing**
  - High kiln fuel consumption
  - Ring formation
  - Refractory damage
  - Chain damage
  - NCG/SOG burning
  - Gaseous/particulate emissions
  - Poor lime quality/availability
  - Overliming/underliming
  - Poor causticizing efficiency
  - Poor mud settling and low solids
  - Clarifier corrosion
  - Process control

- **Liquor Cycle**
  - NPE Accumulation (Cl and K)
  - High deadload
  - Chemical makeup
  - Na and S imbalance
  - High sulphidity operation

Problems Can Be Costly

- **Recovery Boiler Plugging**
  - 0.8 - 1.5 million USD

- **Recovery Boiler Tube Corrosion/Cracking**
  - 5 - 20 million USD

- **Lime kiln ringing**
  - 10,000 - 500,000 USD

- **Environmental impacts**
  - ?? USD
This Course is Designed to Help You To:

- Understand process principles
- Understand possible causes of problems and find solutions to them
- Recognize potential problems that may occur and devise means to prevent them from occurring

Challenges

- Increased economy
  - Increase production capacity
  - Lower operating costs
- Increased environmental protection
  - Increase recovery efficiency
  - Reduce emissions and discharge
- New technologies, sensors and control strategies
- Process simplification