Challenges in Black Liquor Recovery in Modern Kraft Pulp Mills

Honghi Tran
University of Toronto
Toronto, ON, CANADA

Roberto Villarroel
Eldorado Brazil
Sao Paulo, BRAZIL

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Presentation Outline

- Black Liquor
- Operating Issues
- Modern Kraft Mills
- Challenges
- Future Trends
Kraft Pulping Process

Wood + White Liquor (NaOH + Na₂S) → Pulp

155°C, 900 kPa

Lignin, Residual fibre, Chemicals, Water

Weak Black Liquor (8 to 10 t/t pulp)
Black Liquor (as-fired) Composition
(750 liquor samples; Various 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, Btu/lb</td>
<td>5900</td>
<td>5300 – 6600</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>

13.8 MJ/kg
Black liquor is an important, challenging “bioresource” that need to be processed

Kraft pulp mills have been doing just that to recover energy and chemicals
Black Liquor Recovery

Wood Chips → Digester → Bleach Plant

- Green Liquor: Na₂CO₃, Na₂S
- White Liquor: (NaOH, Na₂S)
- Power Boiler
- Lime Kiln
- Causticizer
- Slaker
- Evaporators

(Courtesy Metso Power)
Presentation Outline

- Black Liquor
- Operating Issues
- Modern Kraft Mills
- Challenges
- Future Trends
Common Operating Problems

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

- **Recovery Boilers**
  - Fouling and plugging
  - Corrosion and cracking
  - Low steam production
  - Poor sootblowing efficiency
  - Poor water circulation
  - Smelt-water explosions
  - 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
  - Burners
  - Ring/ball formation
  - Refractory and chains
  - Gaseous/particulate emissions
  - Poor green liquor filterability
  - Poor lime quality/availability
  - Overliming
  - Poor causticizing efficiency
  - Poor mud settling/low solids
  - Clarifier corrosion
  - Process control

- **Liquor Cycle**
  - NPE accumulation (Cl and K)
  - High deadload
  - Na and S imbalance
  - High sulphidity operation
  - Corrosion
Presentation Outline

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Mill Features

- Located mostly in South America, Asia and Scandinavia
- New equipment/facilities and advanced technologies
- Large capacity
- Energy self-sufficient
  - Generate more energy but consume less
- Tight mill closure
Advances in Evap. Technology

- Falling film, plate-type
  - Less susceptible to fouling
- Superconcentrators
  - >80% ds
- Mill waste streams processing

Evaporators installed at a Brazilian mill in 2009
Andritz’s Evaporation System

Digester area:
- Digester Evaporator
- Vapor Re-boiler

Side Streams
- Bio sludge
- ClO₂ plant waste
- Foul condensates
- Effluent/wash waters
- Bleaching effluents
- CTMP filtrates

EVAPORATION
7+ effects

Hot WBL (115...125°C)
Hot steam condensate to RB

Ash treatment / NaCl Purge

Firing liquor at high DS and optimum temperature to RB

CNCG & DNCG to Incineration
Warm/District heating water
Methanol Fuel
High quality secondary condensates

(Courtesy Andritz Inc.)
Advances in RB Technology (1)

- Large firing capacity
- High steam temperature and pressure
  - >500°C and 120 bars
- High solids firing
  - 78 to 85% d.s.
- Burning CNCG and DNCG
Relative Size and Capacity of Recovery Boilers

- 7000 t ds/d, 2010
- 3000 t ds/d, 1990
- 2000 t ds/d, 1986
- 1500 t ds/d, 1976
- 120 t ds/d, 1933

Kari Mäkelä – Metso Power
Advances in RB Technology (2)

- Vertical (multi-level) air systems
  - Low carryover
  - Low NO$_x$
- Sootblowers
  - Fully-expanded nozzles
  - Blowing optimization
  - Using low pressure steam

(Courtesy Andritz Inc.)
Advances in Caust. Technology

- Pressurized filters
  - X filters (green liquor)
  - CD filters (white liquor)
- On-line FT-NIR liquor analyzers and control systems
  - FP Innovations, Metso Automation, etc.
- On-line lime mud solids analyzers
Advances in Kiln Technology

- High lime production capacity
- High mud solids content (>80%)
- Equipped with
  - Lime mud driers (LMD)
  - Efficient product coolers
  - Thermal imaging systems
- Low heat rate (< 6 GJ/t CaO)
Kiln Capacity vs. Startup Year

Lime Kiln at the Eldorado Mill

- 1200 t/d lime
- 5.5 m in diameter x 160 m in length (5 piers)

Courtesy Eldorado and Andritz
Problems in Modern Pulp Mills

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

- Recovery Boilers
  - Fouling and plugging
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- Liquor Cycle
  - NPE accumulation (Cl and K)
  - High deadload
  - Na and S imbalance
  - High sulphidity operation
  - Corrosion
Advanced technologies have helped alleviate many problems in modern kraft mills, but they have also created new challenges....
Kraft pulping process and black liquor
Operating Issues
Modern Kraft Mills
Challenges
Future trends
Tighter Mill Closure

Due to
- High energy and waste disposal costs
- Stringent environmental regulations

Mill responses
- Lowering effluent discharge
- Reclaiming mill waste (ClO₂ generator waste, biosludge, bleaching plant effluents, etc.)

Consequences
- Accumulation of NPEs and impact
- Excess sulphur
- Larger facilities are more susceptible
Non-Process Elements (NPE)

- Elements that do not participate in the pulping process
  - Elements other than Na and S in the liquor cycle
  - Elements other than Ca in the lime cycle

- Common referred NPE:
  - Cl, K
  - Mg, Si, Al, P, Mn, Fe, Cr, Ni, Zn, Pb, Cu, V, Ti, Ba
## Main Sources of NPE

<table>
<thead>
<tr>
<th>Source</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>K, Cl, Si, Al, Mg, Mn, P, Fe, etc.</td>
</tr>
<tr>
<td>Makeup caustic</td>
<td>Cl</td>
</tr>
<tr>
<td>Makeup lime</td>
<td>Si, Al, Mg, P, Fe</td>
</tr>
<tr>
<td>Makeup water</td>
<td>P, Cl</td>
</tr>
<tr>
<td>Additives</td>
<td>Si, Mg</td>
</tr>
<tr>
<td>Refractory bricks</td>
<td>Si, Al</td>
</tr>
<tr>
<td>Corrosion products</td>
<td>Fe, Ni, Cr, Mn</td>
</tr>
<tr>
<td>Biosludge</td>
<td>Si, Mg, P, Al, Cl</td>
</tr>
<tr>
<td>Petcoke</td>
<td>V, Ni</td>
</tr>
</tbody>
</table>
NPE Content in Various Wood Species at a Canadian Mill

mg/kg ds

< 10 ppm: S, B, Cu, Cd, Ti, Cr, V, Li, Co, Ni, As, Pb, Mo
NPE in Eucalyptus

Salmenoja, K. et al.
NPE Removal by GL Clarifiers

Average of 7 Canadian Mills

Removal Efficiency

Mg Mn Fe Zn Pb Al Ba Cu Ni Cr Cd Be Si V P Cl/K
Chloride (Cl) and Potassium (K)

- Accumulate in the liquor cycle due to the high solubility of their compounds.
- Have adverse effects on fouling and corrosion in recovery boilers.
  - Worse for boilers with high furnace and superheated steam temperatures.
- Ash treatment systems for removing Cl & K have become more common.
Several ash treatment systems are now available.

Most rely on effective separation of solids from ash-water slurries:
- Ash with a high carbonate content is much more difficult to separate.

High solids firing and ash treatment lead to:
- High carbonate content in ash
- Excessive S retention (high sulphidity)
Ash E Slurry Settling
(Slurry Conc. = 0.8 kg/L ; T = 85°C)

1 min
5 min
10 min
20 min

0.1 wt% CO₃
Ash C Slurry Settling
(Slurry Conc. = 0.8 kg/L ; T = 85°C )

12.4 wt% CO₃
Effect of CO$_3$ Content on DS
Slurry Conc. = 0.8 kg/L at T= 85°C
Effect of CO$_3$ on Composition of Solids in Ash-Water Slurry

Composition (Wt %)

- Na$_2$SO$_4$
- Burkeite
- Glaserite

CO$_3$ Content in Ash (wt %)

D. Saturnino (2007)
Effect of Silica on Mud Solids

![Graph showing the relationship between SiO₂ content in lime and mud solids for different mills.]

- **Graph legend:**
  - Mill A #1 Kiln
  - Mill A #2 Kiln
  - Mill B #3 Kiln
  - Mill C #2 Kiln

- **Axes:**
  - Y-axis: Mud Solids (wt%)
  - X-axis: SiO₂ Content in Lime (wt%)
Large Pulp Mills

- Often large equipment
  - Recovery boiler: > 5000 t/d BLDS
  - Lime kiln: > 800 t/d lime

- Challenges
  - Sensitive to process disturbance
  - Sensitive to emissions (TRS)
  - Stable operation is vital

- Opportunities
  - Waste stream recovery more economically feasible
  - Great waste energy recovery
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- **Future trends**
  - Alternative fuel use in lime kilns
  - High efficiency recovery boilers
  - Biorefinery
Alternative Fuel Use

- Lime kilns are the major fossil fuel users

- Alternative fuel use is driven by
  - High costs of fuel oil and natural gas
  - “Green” image of biofuel

- Current Status
Types of Alternative Fuels

- Petroleum Coke

- Wood Biofuels
  - Directly fired wood residues (bark, sawdust)
  - Biogas (biomass gasification)
  - Bio-oil (biomass pyrolysis)
  - Precipitated lignin (from black liquor)

- Olein Biofuel
  - Animal fat
Installation at Stora Enso Norrsundet Mill (1985)
Today’s Gasifiers

- Offered by various suppliers
  - Better biomass drying systems

- Types
  - Fluidized bed gasifiers
  - Fixed bed updraft gasifiers
Direct-Fired Lime Kiln System

Lime Kiln

Gasifiers

Dual fuel burner (syngas/natural gas)

Syngas Pressurization fan

Courtesy Nexterra
Bio-Oil

- A mixture of pyrolysis tar, water and pulverized char
- HHV: 16-19 MJ/kg (water content of 20%)
- Atomizes and burns well with similar flame to natural gas
- May be used as fossil fuel substitute

**Challenges:**
- Corrosive (acidic)
- Lack of standard
Precipitated Lignin (LignoBoost Process)

Lignin-lean Liquor
~40%

Liquor from Digester

Wash Liquid
~2 m³/t lignin

Washed Lignin

CO₂

High pH

Low pH

(Courtesy Metso Power)
Precipitated Lignin

- LignoBoost Process
  - Developed and marketed by Inventia and Metso Power

- Properties
  - High heating value
  - Hydrophobic and easy to dry
  - Successful mill trials in Sweden
High Efficiency Recovery Boiler

560-600°C

Wood Gasification

Lime Kiln

+15°C

Gas Cleaning

Combustion Air

160°C

Precipitator

210°C

SCR

Air Preheater

Spent Liquor 85%

125°C

200°C

(Courtesy Andritz Inc.)
High Efficiency Recovery Boiler

560-600°C

Wood Gasification

Gas Cleaning

Lime Kiln

+15°C

Combustion Air

160°C

Precipitator

210°C

Spent Liquor

85%

200°C

(Courtesy Andritz Inc.)
Acknowledgements

- AbitibiBowater
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- DTE Petcoke
- Fibria
- FPInnovations
- International Paper
- Irving Pulp & Paper
- Jammbco
- Kiln Flame Systems
- MeadWestvaco
- Metso Power
- StoraEnso
- Tembec
- Tembec
- Zellstolf Celgar
- NSERC