Improving Black Liquor Processability and Combustibility

Pak Wong
Steam & Steam Power Fall Meeting
December 4, 2007
A mill can achieve significant savings through higher solids firing

Savings for every 1% increase in BLS*, M$/y

* 1000 T/d pulp production basis
High solids (>70%) firing – benefits

- Greater thermal efficiency
- Reduced fouling tendency
- Higher liquor throughput
- Reduced corrosion in the upper furnace
- Lower environmental (sulphur) emissions
High solids (>70%) firing – drawbacks

- Increase in NO$_x$ emissions
- Increase in ESP loading
- Increase in corrosion in the BL header area
- Dramatic rise in black liquor viscosity
What is BL processability?

- BL processability mainly refers to the relative ease by which BL can be:
  - pumped (pumpability)
  - evaporated (evaporability)
  - passed through the guns (firing)
  - sprayed into the recovery boiler (sprayability)
How can we quantify BL processability?

- BL processability can be quantified by:
  - determining BL chemical composition (e.g. to enable the evaluation of the scaling propensity of any given liquor)
  - measuring its rheological (e.g. viscosity) and thermal (e.g. boiling point rise) properties
What is BL combustibility?

- BL combustibility mainly refers to the relative ease by which BL can be burned inside the recovery boiler.

- BL combustibility can be partially quantified by measuring BL rheological properties (e.g. viscosity), swelling volume and higher heating value.

- Other factors besides BL properties will affect BL combustibility (e.g. balancing of combustion air flows, gun and plate angles, bed temperatures, etc.).
Creating forest sector solutions

BL Processability – Viscosity
Viscosity

• Simple definition: resistance to flow
• Technical definition:

\[ \text{Viscosity} = \frac{\text{Shear Stress}}{\text{Shear Rate}} \]
Factors affecting BL viscosity

- Shear rate
- Temperature
- Liquor solids content
- Black liquor composition
  - Wood species (softwood vs. hardwood)
  - Cooking conditions
  - Lignin and carbohydrates content and molecular weight distribution
  - Residual effective alkali (REA) content
  - Tall oil soap content
  - Recycling of bleaching filtrates
Effect of shear rate on BL viscosity

BL is a shear-thinning material
Effect of wood species on BL viscosity

![Graph showing the effect of wood species on BL viscosity.](image)

- **SW#1**
- **SW#2**
- **SW#3**
- **HW#1**

**Legend:**
- **SW – softwood**
- **HW – hardwood**

**Y-axis:** Viscosity at shear rate of 250 s⁻¹, cP

**X-axis:** Temperature, °C
Why do softwood BLs have a higher viscosity than hardwood BLs?

• The viscosity of softwood liquors is typically higher than that of hardwood liquors due to the greater abundance of high molecular weight lignins in softwood liquors.

• In the case of hardwood liquors, polysaccharide content (mainly xylan) was shown to be the primary factor affecting BL viscosity.
Factors Affecting Softwood BL Viscosity
Effect of % BLS on softwood BL viscosity

- Liquor solids, %
- Viscosity at 250 s⁻¹, cP

Graph showing the effect of liquor solids percentage on viscosity at different temperatures:
- 110°C (230°F)
- 115°C (239°F)
- 120°C (248°F)
- 125°C (257°F)
Effect of REA on softwood BL viscosity

69% solids, 2.64% EA, pressurized viscometer: 250 s⁻¹ shear rate
Effect of cooking liquor sulphidity on softwood BL viscosity

Reference: Factors Influencing the Viscosity of Kraft Black Liquor, Soderhjelm, L. and Sagfors, P-E, JPPS (20) 4, 1994
Effect of Soap on the viscosity of a 70% solids BL from a SPF mill
Effect of polysulphide (PS) and PSAQ pulping on BL Viscosity

• Polysulphide and AQ increase pulp yield, decreasing the organic content and calorific value of black liquor
• PS and AQ can accelerate delignification and reduce EA requirements for cooking
• PS and AQ use would be expected to decrease black liquor viscosity at a given solids concentration and temperature, if the REA of the product black liquor is not significantly increased.
Effect of solids on viscosity for Jack Pine BL

Relative viscosity at 100ºC

% Solids

Kraft

PS + AQ
Effect of AQ pulping on viscosity for Pine and spruce BL

![Graph showing viscosity at 125°C with shear rate = 250 s⁻¹, cP.](image)

- **Kraft-AQ REA:** 2.5 – 3.0%
- **Kraft REA:** 1.8- 2.3%
Factors Affecting Hardwood BL Viscosity
Effect of % BLS on hardwood BL viscosity

Viscosity at 250 s\(^{-1}\), cP

Liquor solids, %
Effect of REA on hardwood BL viscosity

![Graph showing the effect of REA on hardwood BL viscosity at 90°C, 100°C, and 110°C.](image)

- **REA, % as Na₂O**
- **Relative viscosity**
- **90°C**
- **100°C**
- **110°C**
Effect of cooking liquor sulphidity on hardwood BL viscosity

Reference: Factors Influencing the Viscosity of Kraft Black Liquor, Soderhjelm, L. and Sagfors, P-E, JPPS (20) 4, 1994
Effect of Pulping Conditions – A Case Study
Effect of cooking conditions on black liquor viscosity

• Mill pulping maple, birch and aspen reported
  – a dramatic drop in evaporator throughput, and
  – liquor firing problems (blackouts)
• Problems were due to high viscosity BL
• BL viscosity increase did not, however, appear related to changes in REA that had earlier caused similar problems at the mill
• Analyses strongly suggested that low sulphidity WL, and high EA charge to the digester, produced viscous black liquors
Effect of REA on hardwood BL viscosity

Viscosity at 105°C and shear rate = 106 s⁻¹, cP

- 69.2% solids
  - 9-Aug-04 sample
- 70.7% solids
  - 27-Sep-05 sample
Effect of green liquor sulphidity and BL REA on firing problems (HW)

![Graph showing the effect of green liquor sulphidity and BL REA on firing problems (HW). The graph displays data points for Sulfidity (normal), Sulfidity (blackout), Effective alkali, and Blackout periods from 5-Aug to 14-Oct. The Blackout Period is highlighted from 2-Sep to 16-Sep.](image)
Summary

- The viscosity of a softwood liquor is usually higher than that of a hardwood liquor
- BL viscosity increases with increasing % BLS
- BL viscosity decreases with increasing temperature
- BL viscosity decreases with increasing pulping liquor sulphidity, especially in the case of hardwood liquors
- There is an optimal REA range for minimum BL viscosity
- BL viscosity usually increases with increasing soap concentration
- Black liquors from PS and AQ pulping have generally lower viscosities at a given temperature and BLS
What is BL swelling volume?

- BL swelling volume is a measure of the volume expansion of BL droplets fired into the recovery boiler during the drying and pyrolysis stages of the combustion process.
- Swelling volume is measured by placing 2 g of BLS in an oven at 400ºC for 5 minutes.
- The swelling volume is estimated by calculating the ratio of the final volume of the swollen BLS over the initial BLS weight (mL/g).
Significance of BL swelling

• The most important liquor variable affecting droplet combustion

• High degree of swelling correlates with good combustion
  – Very high swelling results in liquor droplets being entrained and becoming “fireflies”

• Low swelling
  – Results in slow burning
  – Low swelling liquors tend to put liquor on the bed thus producing smelt of a high carbon content leading to plugging of the smelt spouts
Range of swelling volume for 38 kraft liquors

Factors affecting BL swelling volume

- Wood species
- pH
- Organic:inorganic ratio
- BL activation energy
- Extractives (e.g. soap content > 2.3%)
- Liquor ageing at > 100°C, such as in evaporators
- Crosslinking and polymerization in BL
Effect of pH on BL swelling volume

![Graph showing the effect of pH on BL swelling volume for Kraft and Sulphite processes. The graph plots pH on the x-axis and swelling volume in mL/g dry solids on the y-axis. The graph shows a clear increase in swelling volume as pH increases for both processes, with Kraft showing a more pronounced increase.](image-url)
Effect of activation energy for pyrolysis on BL swollen volume

The swollen volume correlates with the activation energy of pyrolysis for kraft liquor solids from various softwood and hardwood species. All data were obtained from liquor solids with a similar organic/inorganic (O/I) ratio of 1.35 ± 0.1. Eastern softwoods: ○ Jack pine; ◊ balsam fir; □ black spruce; ● mixture. Western softwoods: ◊ red cedar; ◇ Douglas fir; ◈ western hemlock; ◆ mixture. Eastern hardwoods: △ poplar; ▲ white birch; ◆ sugar maple; ◆ mixture.
Effect of soap concentration on BL swelling volume

Swelling volume, mL/g

Soap, % BLS
Effect of lignin removal on BL swollen volume

Summary

- BL swelling volume increases with increasing pH of kraft BL
- BL swelling volume decreases with increasing tall oil soap content, activation energy of pyrolysis, and inorganic dead load
- BL swelling volume is not much affected in the 0-60% lignin removal range