EVAPORATION PRINCIPLES AND BLACK LIQUOR PROPERTIES

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EVAPORATION PRINCIPLES

Slide 1 contains the title of the talk. **Slide 2** shows the outline of topics covered.

Slide 3 presents the amount of black liquor produced at various types of pulp mills.

Slide 3

Kraft Black Liquor Production

- **~ 3000 lb of black liquor solids per ton of air-dried unbleached pulp**
- **Actual value depends on pulping yield:**
  - **High yield processes (e.g., linerboard) ~ 2000**
  - **Dissolving pulps ~ 3500**
- **Oxygen delig. adds 5-10% more solids**

The requirements for black liquor evaporation are given in **Slide 4**.

Slide 4

Evaporation Required to Burn Liquor

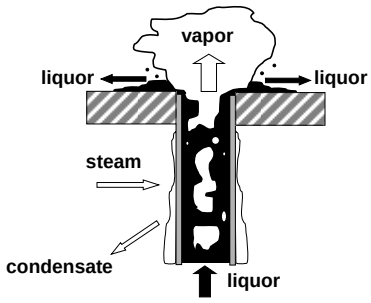
- **Weak BL from washers**
  - **15-20% solids**
  - **80-85% water**
- **BL to recovery boiler**
  - **65-85% solids**
  - **15-25% water**

Weak black liquor from the pulp mill is typically 15% dry solids, or 85% water. Most of this water must be evaporated in order to reach a dry solids level that is adequate for combustion in the recovery boiler. As-fired black liquor dry solids are between about 65% and 85%. During evaporation to this level of dry solids, the liquor releases volatile materials such as sulfur compounds and methanol. These volatiles must be separated from the condensate and gases, and disposed of in an environmentally sound way.

Black liquor evaporators consist of heat exchangers and vapor-liquid separation vessels assembled in units known as "bodies" or "effects." **Slide 5** shows a simplified evaporator with steam condensing on the outside of a steel tube which heats boiling black liquor on the inside. This is an example of the older rising film technology in which vapor expansion inside the tube forces a black liquor film up the tube to a point where the vapor and slightly more concentrated liquor can be separated. The operating principle is much the same as that of an old fashioned percolator coffee pot.

Slide 5

Principle of Evaporation

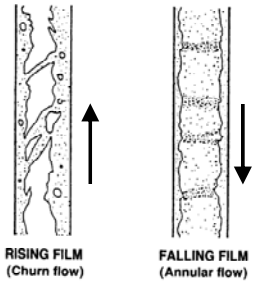


Slide 6 lists the major types of evaporators used for removing water from black liquor. The designs are classified by the liquor flow mode in the heat exchanger and will be discussed in detail in lecture 3-2.

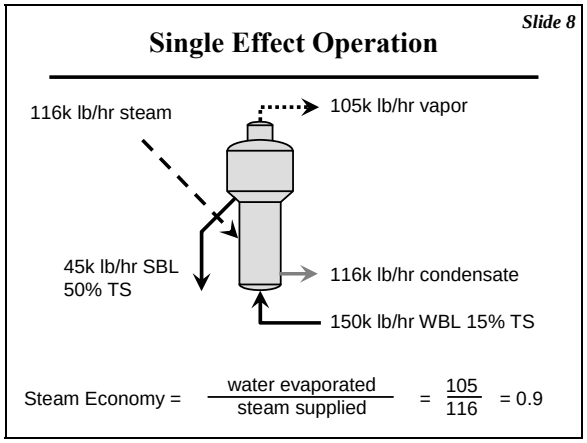
Slide 6

Types of Black Liquor Evaporators

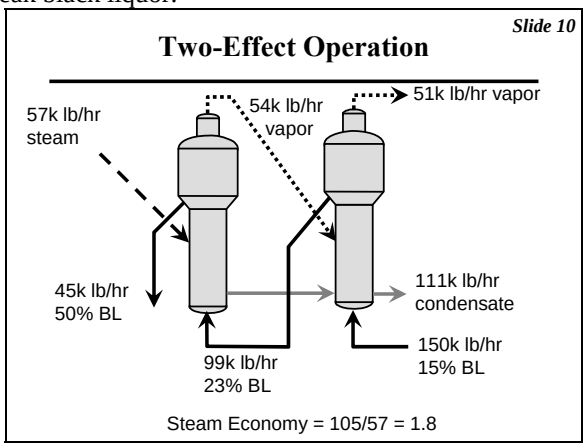
- **Rising Film**
- **Falling Film**
- **Direct Contact**
- **Forced Circulation**



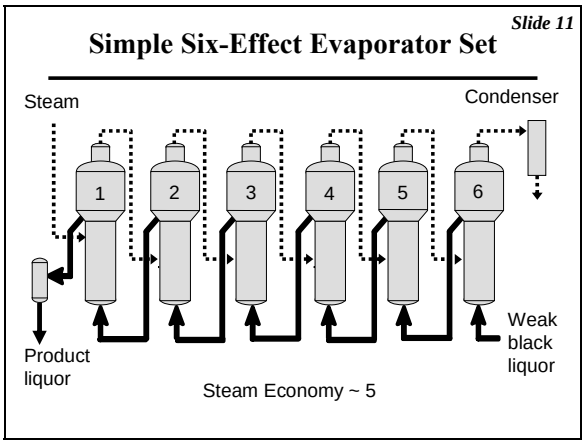
If the heat content of condensing steam was used only once, 100,000 lb of steam would evaporate only 100,000 lb of water from black liquor. Venting, radiation and other losses prevent attaining theoretical efficiency, so that thermal efficiency in a single evaporator effect is only about 90%. **Slide 8** gives a material and energy balance for a single effect and introduces the concept of steam economy.



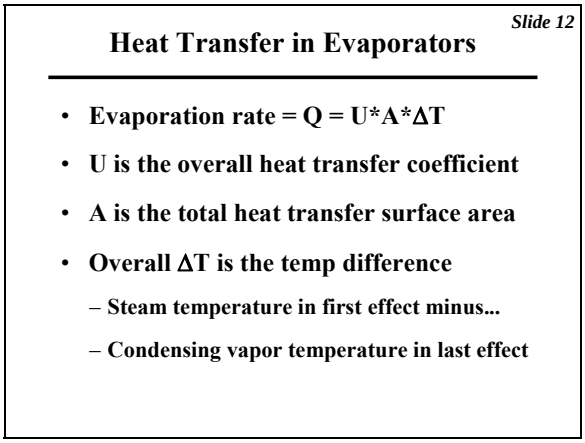
Economic operation dictates the multiple effective use of the heat content of steam and so several evaporator bodies are combined in a system in which the vapor released from boiling liquor in one effect is condensed to provide heat for boiling liquor in another effect. **Slide 10** provides values illustrating how combining effects reduces the steam required to evaporate a fixed amount of water from weak black liquor.



Slide 11 shows a typical industrial configuration of rising film evaporators where approximately 500,000 lb of water vapor can be removed from black liquor by condensing 100,000 lb of steam. Design and operation of various types of multiple effect evaporators are given in lecture 3-2.



As with all indirect heat exchangers, the expression for overall heat transfer between the condensing steam and the black liquor is the basic relationship shown in **Slide 12**. The heat flow depends on the overall heat transfer coefficient, U, the heat transfer surface area, A, and the temperature difference between the steam and the liquor ΔT. The evaporator designer controls the amount of area, which is often dictated by the values of U and ΔT that can be obtained for a given evaporator technology and liquor properties.



BLACK LIQUOR PROPERTIES

Slide 13 indicates that there are several physical and thermal properties that are important to black liquor evaporator design and operation.

Slide 13

Black Liquor Properties

- **Basis of evaporation equipment design**
- **Changes in liquor cycle chemistry can impact evaporator performance if properties depart from design values**
  - **Viscosity**
  - **Boiling point rise**
  - **Concentration of scaling species**

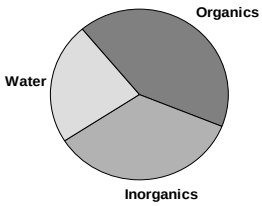
Slide 14 shows that black liquor is typically about one-third inorganic and two-thirds organic material. As the liquor dry solids increases during evaporation, some of the inorganic species exceed their solubility limit and can deposit as scale on the evaporator heat transfer surfaces.

Rising film evaporator product solids content is often monitored by measuring its specific gravity. As shown in **Slide 15**, there are concerns with applying this technique to liquors over 50% solids.

Slide 14

Black Liquor Composition

Wet basis



Dry solids basis

Alkali lignin, wt-%	30 - 45
Wood acids & Polysaccarides	30 - 45
Inorganics, salts	30 - 45
Resins, fatty acids	3 - 5
Methanol	~1

Slide 15

Black Liquor Specific Gravity

- **Important for performance calculations**
- **ºBaumé (hydrometer up to 50% solids), must be corrected for temperature**

SG of BL @ 60ºF / water @ 60ºF = 145/(145 - ºBé)

- **Solid content inferred from ºBaumé, but correlation changes with wood species!**

Slide 16 provides a useful correlation for determining black liquor density as a function of solids and temperature. This (and other) correlations are within ±2% of measured values up to 50% solids. The density examples with feed and product liquor illustrate the importance of calculating mass flows rather than relying on volumetric flow changes. Concerns about extrapolating this correlation are also given in the slide.

Slide 16

Black Liquor Density Correlations

- **Correlation for ≤ 50% BLS, T ≤ 100ºC**

ρ, *g/cm3 = 1.007 + 0.006*(%S) - 0.000495* (TºC)*

- **Ex: 15% BLS, 82ºC (180ºF) > 1.06 g/cm3**
- **Ex: 49% BLS, 93ºC (200ºF) > 1.26 g/cm3**
- **Non-linear behavior at high solids**
- **Extrapolation to firing conditions ± 10%**

Slide 17 gives three thermal properties needed to complete energy balance calculations around black liquor evaporators. These are not greatly affected by black liquor composition and detailed information on these properties can be found in reference textbooks.

Slide 17

Black Liquor Thermal Properties

- **Thermal conductivity correlation ± 4%**

k, *W/mºC* $= 0.58 + 1.44\times10^{-3}$ *(TºC)* $- 3.35\times10^{-3}$ *(%S)*

- **Specific heat (Cp) varies with solids & temp.**
  - **2700-3900 J/kg /°C (0.65-0.95 Btu/lb/°F)**
- **Heat of vaporization ~2325 KJ/kg (1000 Btu/lb)**

Slide 18 shows a table of black liquor viscosity for conditions typical of those in an evaporator set. Two reference viscosities are also given for water and motor oil.

Slide 18

Typical Black Liquor Viscosities

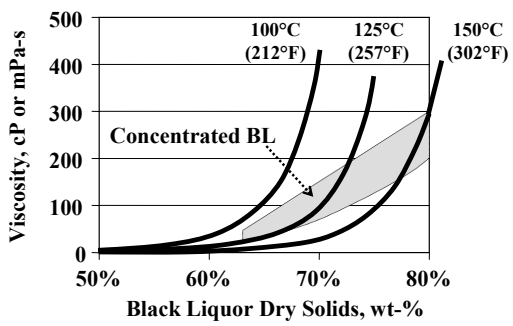
- **Viscosity of room temp water ~ 1 cp (mPa-s)**
- **Viscosity of SAE 30 oil at 80°F ~ 200 cp (mPa-s)**

BL Dry Solids	Temp., °F	Temp., °C	Viscosity, cP
18%	150	66	1.0
21%	180	82	0.9
26%	200	93	1.0
34%	230	110	1.3
42%	240	116	2.3
51%	250	121	4.9
70%	260	127	88

Slide 19 illustrates how black liquor viscosity depends on dry solids content and temperature for "typical" black liquor. Above 60% solids, viscosity is a very strong function of solids content. The range of black liquor viscosity for typical concentrated liquor is indicated on the plot. Though some fairly high values of viscosity can be reached in high-solids concentrators and as-fired liquor, the viscosity of black liquor below 50% solids is relatively low.

Slide 19

Black Liquor Viscosity vs. Solids



Slide 20 indicates that black liquor is a viscous material whose inherent viscosity is a complex, and mostly unknown, function of pulping conditions.

Slide 20

What Determines Black Liquor Viscosity?

- **Total solids content & Temperature**
- **Wood species & cooking conditions**
- **Residual alkali / pH**
- **Correlations exist, but actual black liquor viscosity differs ± 400%!!**
  - **Viscosity must be measured for evap design**

Slide 21 shows that variations in viscosity of the black liquor can have a strong effect on U-values, which can affect evaporator performance relative to design conditions. This applies to all types of evaporators, particularly falling film units operating at high total solids contents.

Another black liquor property that strongly affects evaporator operation is the boiling point rise (BPR) as described in **Slide 22**.

Slide 21

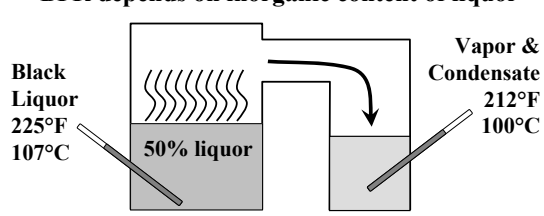
Impacts of Viscosity

- **Evap design affected greatly by viscosity**
  - **Heat transfer coefficient (U value)**
  - **Power usage in units with recirculation pumps**
- **Evaporator capacity can be affected by changes in viscosity, e.g. wood species**
  - **Viscosity up 5 fold, U value down 50%**

Slide 22

Black Liquor Boiling Point Rise

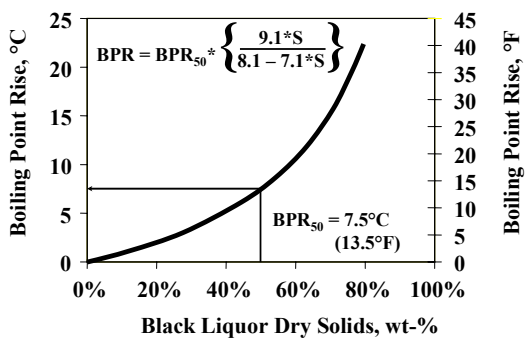
- **BL boils at temps above water boiling point**
- **Boiling point rise (BPR) increases with solids**
- **BPR depends on inorganic content of liquor**



Aqueous solutions can have a boiling point above that for pure water. The difference between the boiling point of the solution and that for water is the boiling point rise. For black liquor, it is the inorganic content that affects BPR the most. **Slide 23** shows BPR as a function of liquor dry solids for "typical" black liquor.

Slide 23

Boiling Point Rise vs. Solids



BPR rises quickly with increased liquor dry solids. Equations for BPR are often specified in terms of the BPR at 50% dry solids, BPR_{50}. BPR_{50} is typically about 7 to 8°C (12.5 to 14.5°F). The curve in the slide is specifically for a BPR_{50} of 7.5°C.

The boiling point rise is especially important in black liquor evaporation because it reduces the available temperature differential for heat transfer. **Slide 24** tabulates the dry solids contents and BPR values in each effect of a multiple effect evaporator. The impact of BPR in each effect is to cumulatively reduce the overall ΔT for the evaporator set. This will be discussed further in lecture 3-2.

Slide 24

BPR at Each Effect

Effect #	BL Dry Solids	BPR, °C	BPR, °F
6	18%	1.8	3.2
5	21%	2.2	3.9
4	26%	2.8	5.1
3	34%	4.1	7.3
2	42%	5.6	10.1
1	51%	7.8	14.0
Total		24.3	43.7

- **Total $\Delta T = T_{steam} - T_{condenser} - BPR$ (total)**

The importance of BPR to evaporator design and operation is summarized in **Slide 25**.

Slide 25

Impacts of BPR

- **Evap design affected greatly by BPR**
  - **Cumulative impact in multiple effect units**
- **Evaporator capacity can be affected by changes in BPR, e.g. alkali/wood charge**
  - **Higher alkali charge can result in higher inorganic content and higher BPR**

Changes in black liquor viscosity and boiling point rise are not the only black liquor properties that affect evaporator performance. Black liquor contains a substantial fraction of sodium, and smaller amounts of calcium, aluminum, silicon, carbonate, and sulfate. Each of these can contribute to deposits of scale materials on the heat transfer surfaces of evaporators. **Slide 26** shows a typical elemental composition for kraft black liquor.

Slide 26

Typical Black Liquor Composition

Major

Element		wt-% BLS
Carbon	C	35.0%
Hydrogen	H	3.3%
Oxygen	O	35.7%
Sodium	Na	19.7%
Potassium	K	1.6%
Sulfur	S	4.0%

Minor

Element		wt-% BLS
Calcium	Ca	600 ppm
Aluminum	Al	50 ppm
Silicon	Si	700 ppm
Iron	Fe	150 ppm
Carbonate	CO_3	8%
Sulfate	SO_4	3%

Slide 27 introduces scale deposits in black liquor evaporators; the subject of lecture 3-3 in this course.

Slide 27

Black Liquor Evaporator Scaling

- **Na, $SO_4^=$, $CO_3^=$ cause soluble Na scale**
- **Dissolved Ca causes insoluble calcium scale**
- **Al and Si cause aluminosilicate scale**
- **Organics increase scaling and fouling rate**

Scaling reduces U values and can rob available heat-transfer area by plugging tubes

The inorganic materials are often the cause of scale formation, but the organic fraction of black liquor can also contribute to the fouling rate of these units. The composition of black liquor changes whenever makeup chemicals are added to it. This affects the inorganic composition and the scaling potential.

SUMMARY

Slide 28 summarizes this introduction to black liquor evaporation and properties. Three good references for additional information are listed below.

Slide 28

Summary

- **Weak BL is ~ 15% dry solids**
- **As-fired BL must be 65% to 85% solids**
- **Variation in BL properties relative to design values affects evaporator performance**
  - **Higher viscosity reduces U values at high solids**
  - **Higher boiling point rise reduces available ΔT**
  - **Changes in liquor components can foul heater surfaces**

ACKNOWLEDGEMENT

Manuscript and presentation slides were by Christopher L. Verrill.

FURTHER READING

Grace, T. M., Black Liquor Evaporation, in Pulp and Paper Manufacture, Volume 5-Alkaline Pulping, Joint Textbook Committee of the Paper Industry, Atlanta GA (1989).

Venkatesh, V, and Nguyen, X. N., Evaporation and Concentration of Black Liquor, in Chemical Recovery in the Alkaline Pulping Process, TAPPI Press, Atlanta (1992).

Frederick, W. J. Jr., Black Liquor Properties, Chapter 3 of Kraft Recovery Boilers, Adams, T. N., Ed., TAPPI Press, Atlanta, pp. 59-99 (1997).