BLACK LIQUOR PROPERTIES AND EVAPORATION PRINCIPLES

W. J. Frederick, Ph.D.
Principal
Table Mountain Consulting
Golden, CO 80403

David T. Clay, Ph.D.
Senior Process Consultant
Jacobs Engineering
Lake Oswego, OR 97035

BLACK LIQUOR PROPERTIES

Black liquor has its own unique physical and chemical properties. These properties control how it performs during kraft chemical recovery, and are important in design of process equipment for used in chemical recovery plants.

Figure 1 indicates that there are several physical and thermal properties that are important to black liquor evaporator design and operation.

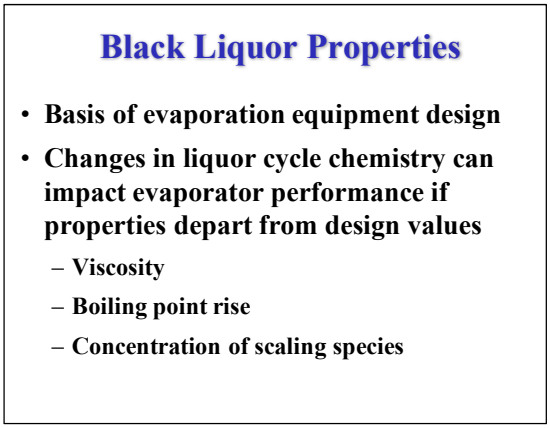


Figure 1. Black liquor properties for design of evaporation equipment.

Figure 2 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.

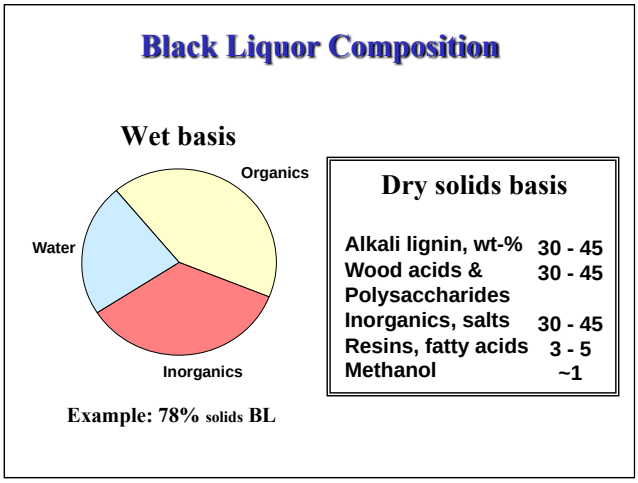


Figure 2. Nominal composition of black liquor.

Evaporator product solids content is often monitored by measuring its specific gravity. As shown in **Figure 3**, there are concerns with applying this technique to liquors over 50% solids.

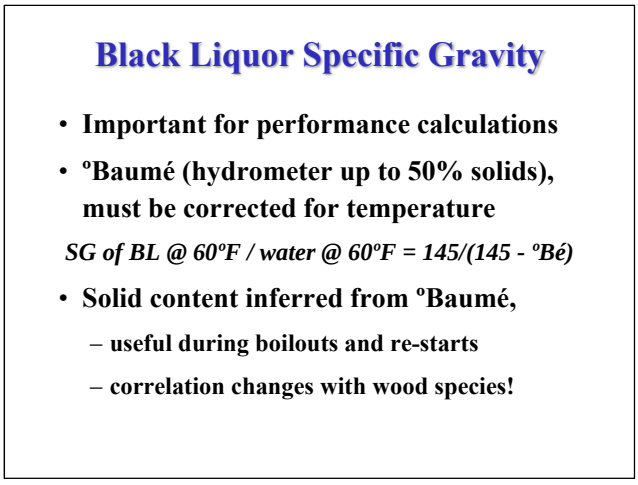


Figure 3. Interpreting black liquor specific gravity.

Figure 4 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.

Black Liquor Density Correlations

- **Correlation for ≤ 50% BLS, T ≤ 100°C**

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

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

Figure 4. Estimating black liquor density.

Figure 5 gives four thermal properties needed to complete a material and energy balance (performance calculations) for black liquor evaporators. These, except for viscosity, are not greatly affected by black liquor composition. Viscosity is significantly affected by black liquor composition, including its water content. Detailed information on these properties can be found in the referenced textbooks.

Black Liquor Thermal Properties

- **Properties for detailed material and energy balances are in references listed in the paper.**
  - **Heat of vaporization**
  - **Specific heat**
  - **Thermal conductivity ***
  - **Viscosity ***

**** Only if heat transfer coefficients are calculated from first principals.***

Figure 5. The four thermal properties needed to complete a material and energy balance (performance calculations) for black liquor evaporators.

Figure 6 is 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.

Black Liquo Viscosity through 7 Effects

- **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

Figure 6. Change in black liquor viscosity with temperature and dry solids content through 7 effects in an evaporator set.

Figure 7 illustrates how black liquor viscosity depends on dry solids content and temperature for "typical" black liquor in a concentrator set. Above 60% dry solids content, viscosity is a very strong function of dry solids content. The range of black liquor viscosity for typical concentrated liquor is indicated on the plot. Black liquor viscosity near 80 wt-% dry solids content approaches 300 cP, an upper limit of pumpability for centrifugal pumps.

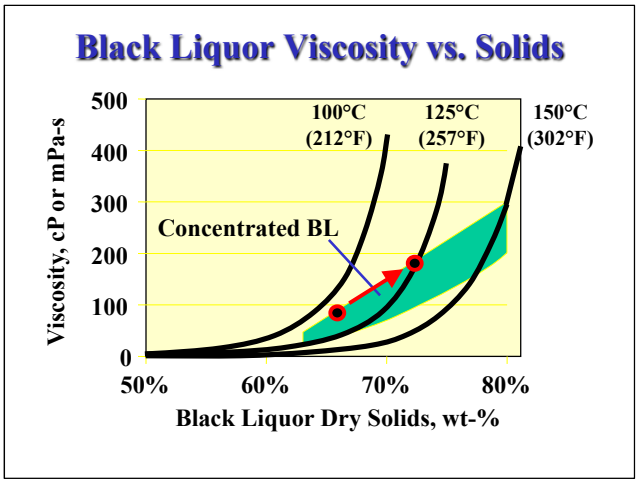


Figure 7. Increase in black liquor viscosity at temperatures and dry solids content through a concentrator set.

Black liquor is a viscous material whose inherent viscosity is a complex function of its chemical composition of its chemical composition and pulping conditions. **Figure 8** shows how the viscosity of black liquors from different wood species vary with dry solids content. At 75 wt% dry solids content, the range of viscosity among the six black liquors shown is a factor of 50.

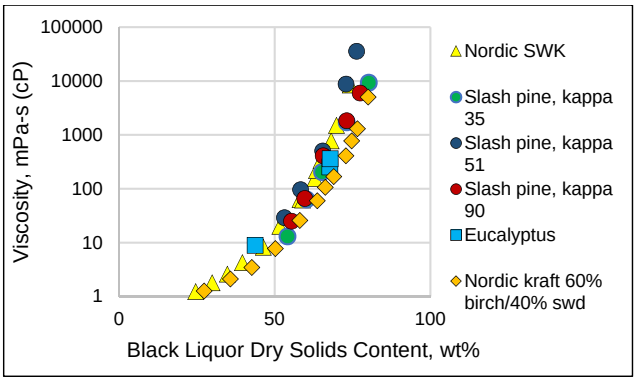


Figure 8. Variation of black liquor viscosity with dry solids content for six different black liquors.

Figure 9 shows that viscosity of black liquor from wood pulped to different kappa numbers goes through a maximum between 40 and 60 kappa.

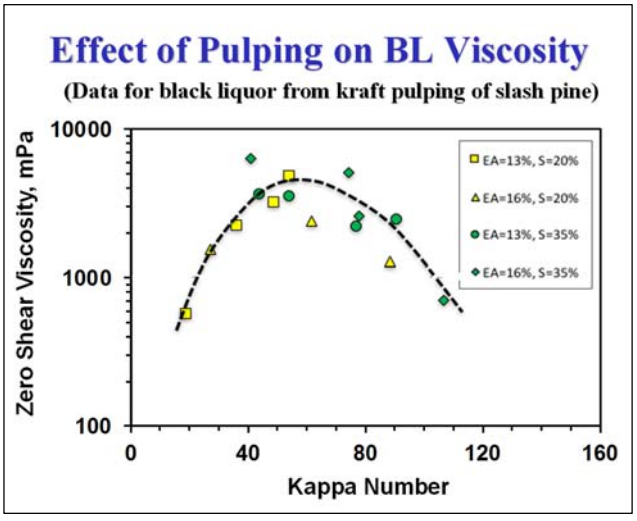


Figure 9. How pulping conditions determine the viscosity of black liquor produced from slash pine.

Figure 10 shows that the viscosity of black liquor depends strongly on its residual alkali content. Viscosity goes through a minimum at 4% RAA as wt-% Na_2O on black liquor solids, equivalent to 6 g/L RAA at 14 wt% dry solids content.

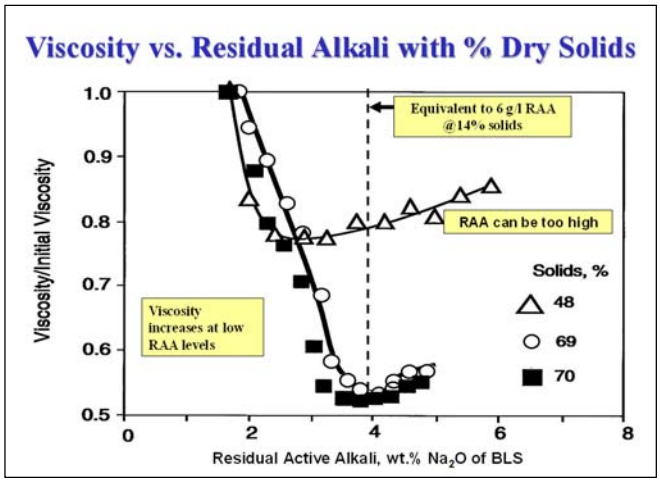


Figure 10. The impact of the residual alkali content of black liquor on its viscosity.

Figure 11 summarizes what determines the values of black liquor viscosity

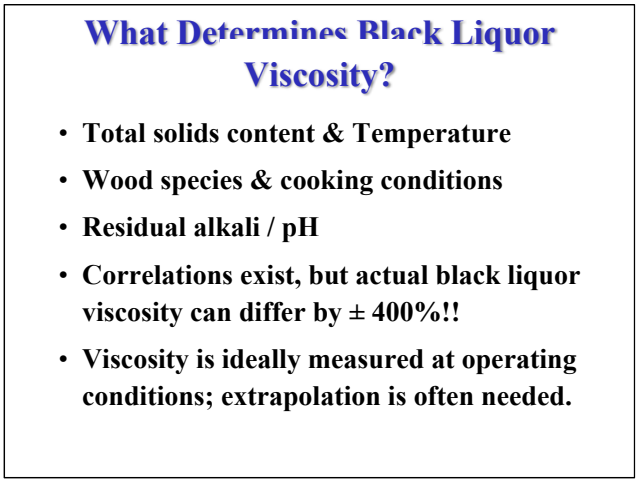


Figure 11. Factors that determine black liquor viscosity.

Figure 12 shows that variations in viscosity of a black liquor can have a strong effect on heat transfer coefficients (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.

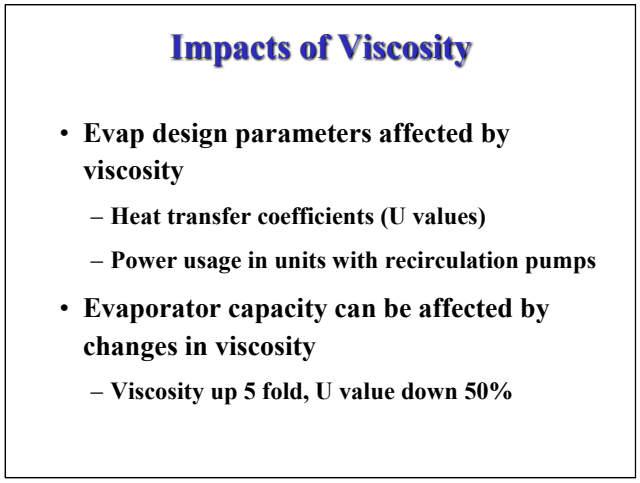


Figure 12. Impact of viscosity on evaporator and concentrator performance.

Another black liquor property that affects evaporator design, especially at high percent solids, is the boiling point rise (BPR) as described in **Slide 13**.

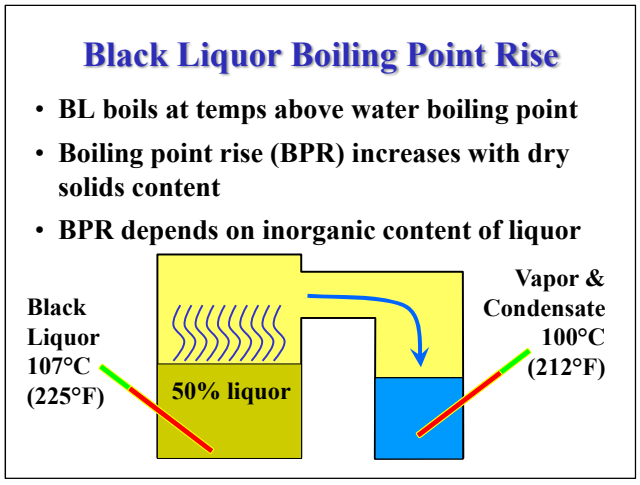


Figure 13. black liquor boiling point rise.

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. **Figure 14** shows BPR as a function of liquor dry solids content for "typical" black liquor.

BPR rises quickly with increased liquor dry solids content. 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.

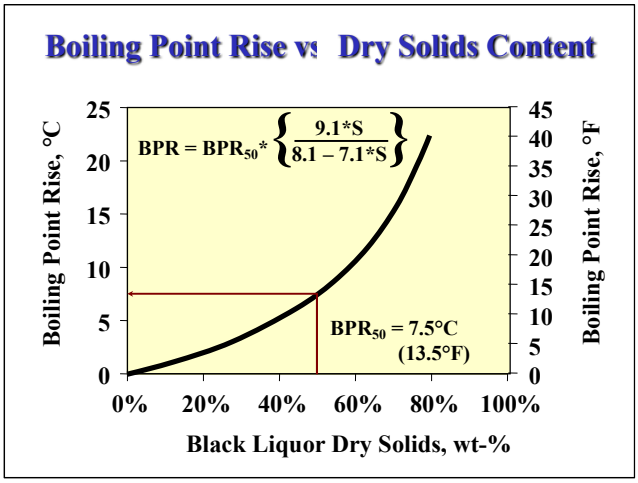


Figure 14. Boiling point rise versus dry black liquor solids content.

The boiling point rise is especially important in black liquor evaporation because it reduces the available temperature difference for heat transfer. **Figure 15** tabulates the dry solids contents and BPR values in each effect of a 6-effect 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 Section 3-2.

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 $\Delta T = T_{steam} - T_{condenser} - \Sigma BPR$

Figure 15. Individual and cumulative boiling point rises for a 6-effect multiple effect evaporator.

The importance of BPR to evaporator design and operation is summarized in **Figure 16**.

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**

Figure 16. Impacts of BPR on evaporator design and capacity.

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, moderate amounts of carbonate and sulfate, and smaller amounts of calcium, silicon, and aluminum. Each of these can contribute to deposits of scale materials on the heat transfer surfaces of evaporators. **Figure 17** shows a typical elemental composition for kraft black liquor.

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
Chloride	Cl	0.5%
Calcium	Ca	600 ppm
Aluminum	Al	50 ppm
Silicon	Si	700 ppm
Carbonate	CO_3	4%
Sulfate	SO_4	3%

Figure 17. Elemental composition of a typical black liquor.

Figure 18 introduces scale deposits in black liquor evaporators; the subject of Section 3-3 in this course.

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

Figure 18. Types of black liquor evaporator scaling.

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.

EVAPORATION PRINCIPLES

Figure 19 below presents the amount of black liquor produced at various types of pulp mills.

Black Liquor Production

~ 3000 lb of black liquor solids per ton air-dried unbleached pulp

Figure 19. Typical amount of black liquor dry solids produced per ton of ADUP.

The requirements for black liquor evaporation are given in **Figure 20** below.

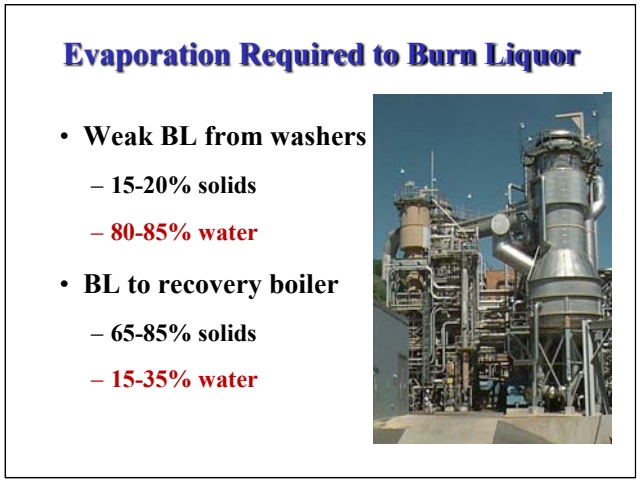


Figure 20. Evaporation required to produce black liquor for firing.

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. Some volatiles are non-condensible gases that must be separated from the condensate and other 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." **Figure 21** shows a simplified evaporator diagram 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.

Figure 21. Illustration of boiling and vapor and liquid transport in a rising film evaporator.

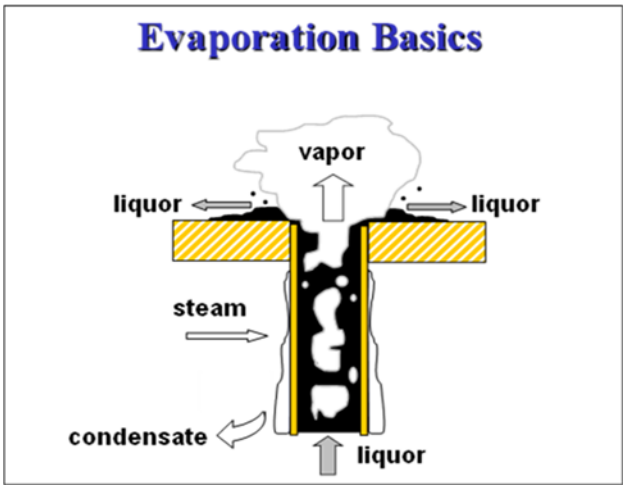


Figure 21. Boiling and vapor and liquid transport in a rising film evaporator.

Figure 22 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 Section 3-2.

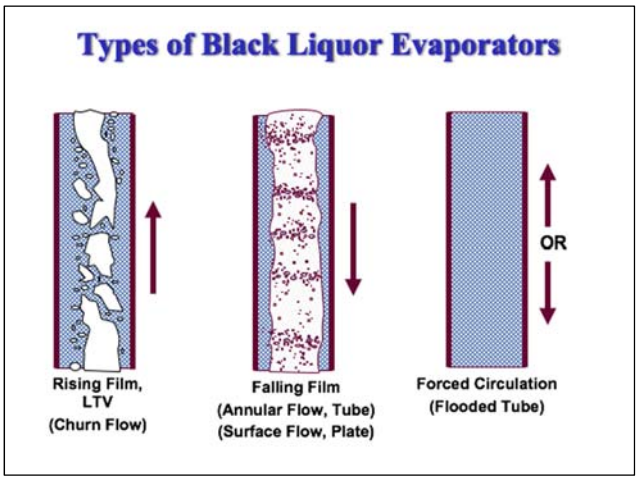


Figure 22. Flow modes in the three generic types modern of black liquor evaporators.

Figure 23 states that 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. Sensible heating, venting, radiation and other losses prevent attaining theoretical efficiency, so that thermal efficiency in a single evaporator effect is only about 90%.

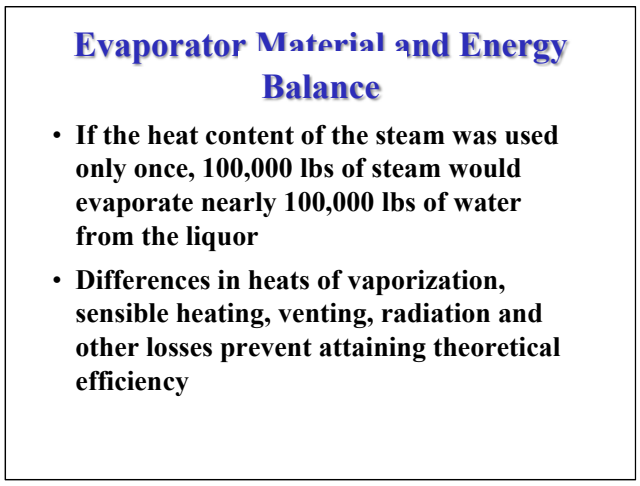


Figure 23. The concept of energy reuse in an evaporator.

Figure 24 gives a material and energy balance for a single effect and introduces the concept of steam economy.

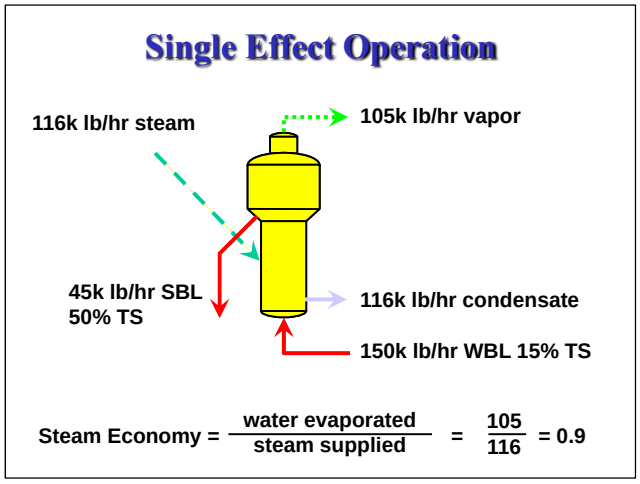


Figure 24. Material and energy balance for a single effect evaporator.

Figure 25 notes that economic operation dictates multiple effect use of the heat content of steam. Several evaporator bodies are combined into a system in which the vapor released from boiling liquor in one effect is condensed to provide heat for boiling liquor in a subsequent (lower pressure) effect. This figure provides values illustrating how combining effects reduces the steam required to evaporate a fixed amount of water from weak black liquor. Fresh steam is supplied to one body. If both bodies were supplied fresh steam, it would be one-effect operation with two bodies.

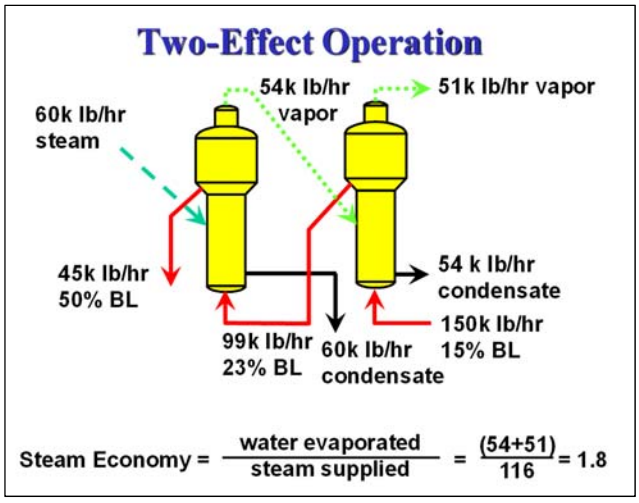


Figure 25. Material and energy balance for a 2-effect evaporator.

Effects are integrated together as in **Figure 25** but with more bodies, to form multiple effect evaporators and concentrators. Design and operation of several types of multiple effect evaporators and concentrators will be discussed in Section 3-2.

The liquor heating section in evaporators and concentrators is a heat exchanger. As with all indirect heat exchangers, the expression for heat transfer between the condensing steam and the black liquor is the relationship shown in **Figure 26**. 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 heat transfer surface area, which is mainly dictated by the values of U and ΔT that can be obtained in a body for a given evaporator technology and liquor properties.

Heat Transfer in Evaporator Body

- **Evaporation rate = Q = U*A*ΔT**
- **U is the heat transfer coefficient**
- **A is the heat transfer surface area**
- **ΔT for a body is the temperature difference:**
  - **Condensing steam/vapor temperature minus...**
  - **Outlet black liquor temperature from that body**

Figure 26. Heat transfer rate equation for an evaporator body.

SUMMARY

Figure 27 summarizes this introduction to black liquor properties and evaporation principles. Three good references for additional information are listed below.

Summary

- **Weak BL is ~ 15% dry solids**
- **As-fired BL range: 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 composition can scale or foul heater surfaces**

Figure 27. Summary.

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).

Blair, M.G and E.L. Peffer, Thermal-Density Coefficients and Hydrometer Correction Tables, Research Paper RP1612, Journal *of Research of the National Bureau of Standards*, Volume 33, *November 1944.* http://nvlpubs.nist.gov/nistpubs/jres/33/jresv33n5p341_a1b.pdf

Table 1. Blair, M.G and E.L. Peffer, *Hydrometer Correction Tables*

TABLE 5.—*Hydrometer correction data*

Reduction of observed specific gravities to specific gravities at 60°/60° F.

Observed temperature	Observed specific gravity						
	1.0000	1.0200	1.0400	1.0600	1.0800	1.1000	1.1200
	Corresponding specific gravity at 60°/60° F						
°F							
50		1.0193	1.0391	1.0590	1.0788	1.0987	1.1186
51		1.0193	1.0392	1.0591	1.0790	1.0988	1.1187
52		1.0194	1.0393	1.0592	1.0791	1.0989	1.1188
53		1.0194	1.0394	1.0593	1.0792	1.0991	1.1190
54		1.0195	1.0395	1.0594	1.0793	1.0992	1.1191
55		1.0196	1.0395	1.0595	1.0794	1.0993	1.1192
56		1.0197	1.0396	1.0596	1.0796	1.0995	1.1194
57		1.0197	1.0397	1.0597	1.0797	1.0996	1.1195
58		1.0198	1.0398	1.0598	1.0798	1.0997	1.1197
59		1.0199	1.0399	1.0599	1.0799	1.0998	1.1198
60	1.0000	1.0200	1.0400	1.0600	1.0800	1.1000	1.1200
61	1.0001	1.0201	1.0401	1.0601	1.0801	1.1001	1.1202
62	1.0001	1.0202	1.0402	1.0602	1.0803	1.1003	1.1204
63	1.0002	1.0203	1.0403	1.0604	1.0804	1.1004	1.1205
64	1.0003	1.0204	1.0404	1.0605	1.0806	1.1005	1.1207
65	1.0004	1.0205	1.0406	1.0606	1.0807	1.1008	1.1208
66	1.0005	1.0206	1.0407	1.0608	1.0808	1.1009	1.1210
67	1.0006	1.0207	1.0408	1.0609	1.0810	1.1011	1.1212
68	1.0007	1.0208	1.0409	1.0610	1.0812	1.1013	1.1214
69	1.0008	1.0210	1.0411	1.0612	1.0813	1.1014	1.1216
70	1.0010	1.0211	1.0412	1.0613	1.0815	1.1016	1.1218
71	1.0011	1.0212	1.0413	1.0615	1.0817	1.1018	1.1220
72	1.0012	1.0213	1.0415	1.0616	1.0818	1.1020	1.1221
73	1.0013	1.0215	1.0416	1.0618	1.0820	1.1022	1.1223
74	1.0014	1.0216	1.0418	1.0620	1.0822	1.1024	1.1225
75	1.0015	1.0217	1.0419	1.0621	1.0823	1.1026	1.1227
76	1.0017	1.0219	1.0421	1.0623	1.0825	1.1027	1.1229
77	1.0018	1.0220	1.0422	1.0625	1.0827	1.1029	1.1231
78	1.0019	1.0222	1.0424	1.0626	1.0829	1.1031	1.1233
79	1.0021	1.0223	1.0426	1.0628	1.0830	1.1033	1.1236
80	1.0022	1.0225	1.0427	1.0630	1.0832	1.1035	1.1238
81	1.0024	1.0226	1.0429	1.0632	1.0834	1.1037	1.1240
82	1.0025	1.0228	1.0430	1.0634	1.0836	1.1039	1.1242
83	1.0027	1.0230	1.0432	1.0636	1.0838	1.1041	1.1244
84	1.0028	1.0231	1.0434	1.0638	1.0840	1.1043	1.1246
85	1.0030	1.0233	1.0436	1.0639	1.0842	1.1046	1.1248
86	1.0031	1.0234	1.0438	1.0641	1.0844	1.1048	1.1251
87	1.0033	1.0236	1.0439	1.0643	1.0846	1.1050	1.1253
88	1.0035	1.0238	1.0441	1.0645	1.0848	1.1052	1.1256
89	1.0036	1.0240	1.0443	1.0647	1.0850	1.1054	1.1258
90	1.0038	1.0241	1.0445	1.0649	1.0852	1.1057	1.1260
91	1.0040	1.0243	1.0447	1.0651	1.0855	1.1059	1.1262
92	1.0041	1.0245	1.0449	1.0653	1.0857	1.1062	1.1265
93	1.0043	1.0247	1.0451	1.0655	1.0859	1.1064	1.1267
94	1.0045	1.0249	1.0453	1.0657	1.0861	1.1066	1.1270
95	1.0047	1.0251	1.0455	1.0659	1.0864	1.1068	1.1272
96	1.0048	1.0253	1.0457	1.0662	1.0866	1.1070	1.1274
97	1.0050	1.0255	1.0459	1.0664	1.0868	1.1073	1.1277
98	1.0052	1.0257	1.0461	1.0666	1.0870	1.1075	1.1280
99	1.0054	1.0259	1.0464	1.0668	2.0872	1.1078	1.1282
100	1.0056	1.0261	1.0466	1.0671	1.0875	1.1080	1.1285