Black Liquor and Evaporators

Properties, Principles and Equipment

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2021 TAPPI Kraft Recovery Course

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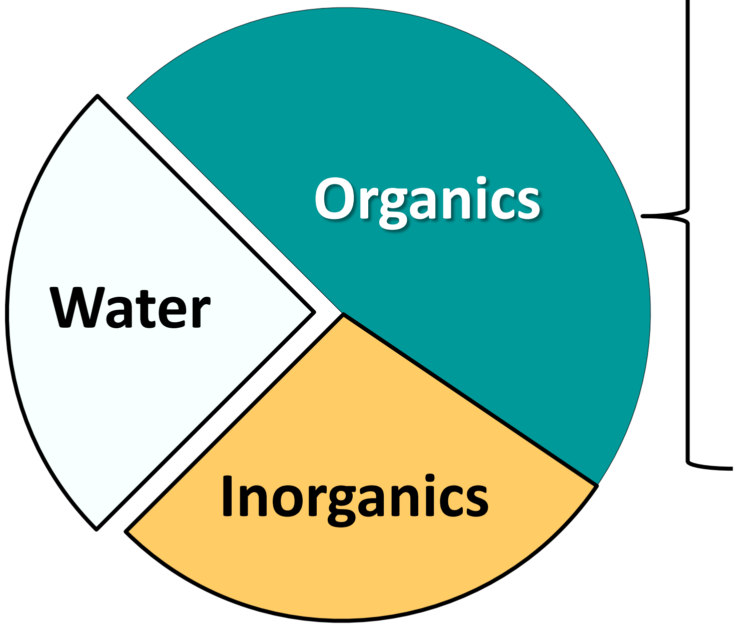
Outline

- **Black liquor composition**
- **Black liquor properties**
  - Boiling point rise
  - Viscosity
  - Density / specific gravity
  - Target properties
- **Evaporator equipment**
  - Principles and heat transfer
  - Multiple effect evaporation
  - Evaporator types
  - Materials of construction

Black Liquor Composition
(An example & 75% dry solids)

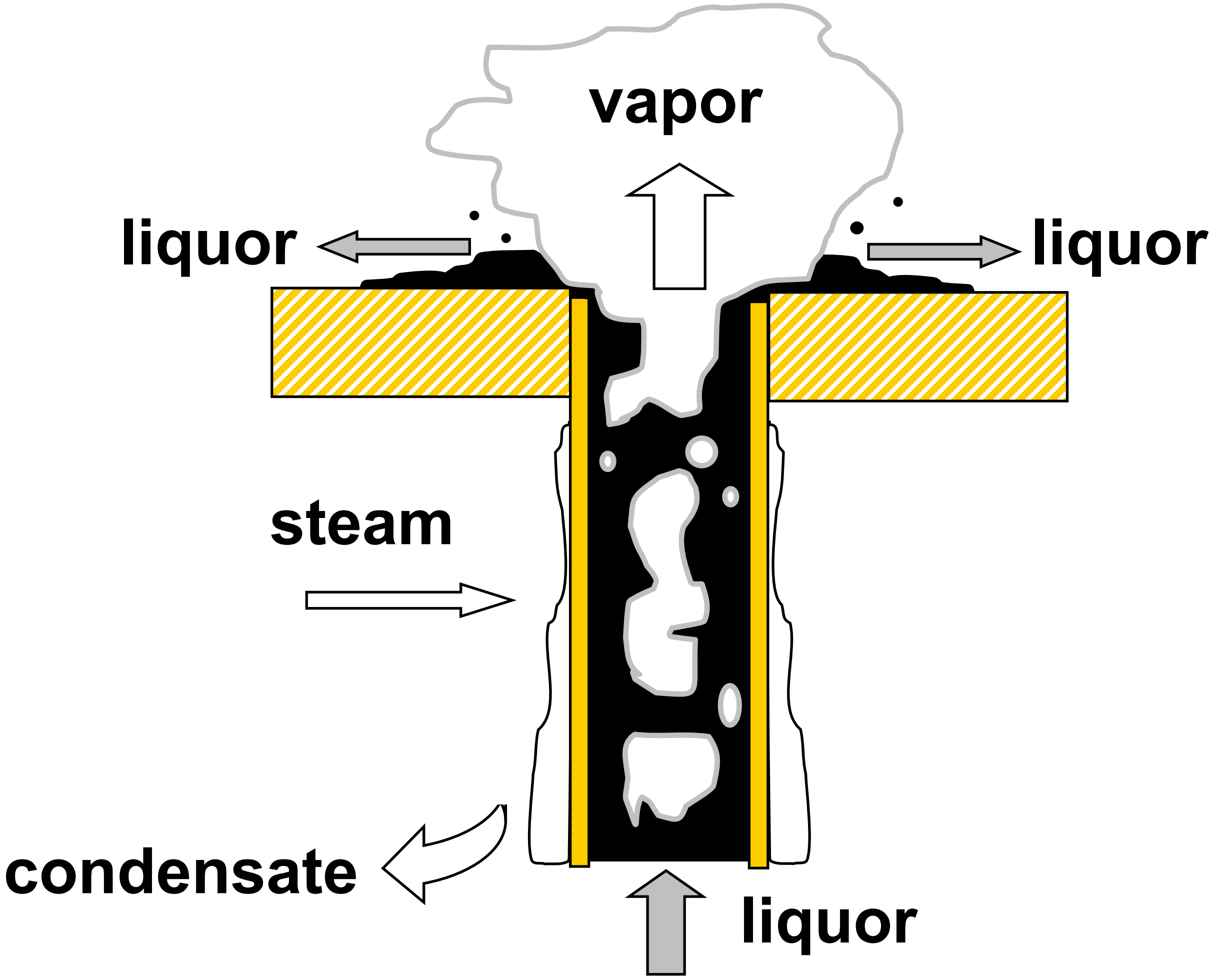


Components	wt% ds
Alkali lignin, wt-%	30 - 45
Wood acids, polysaccharides	30 - 45
Resins, fatty acids	3 - 5
Methanol	~ 1
Inorganic, salts	30 - 45

Black Liquor Dry Solids - Inorganics

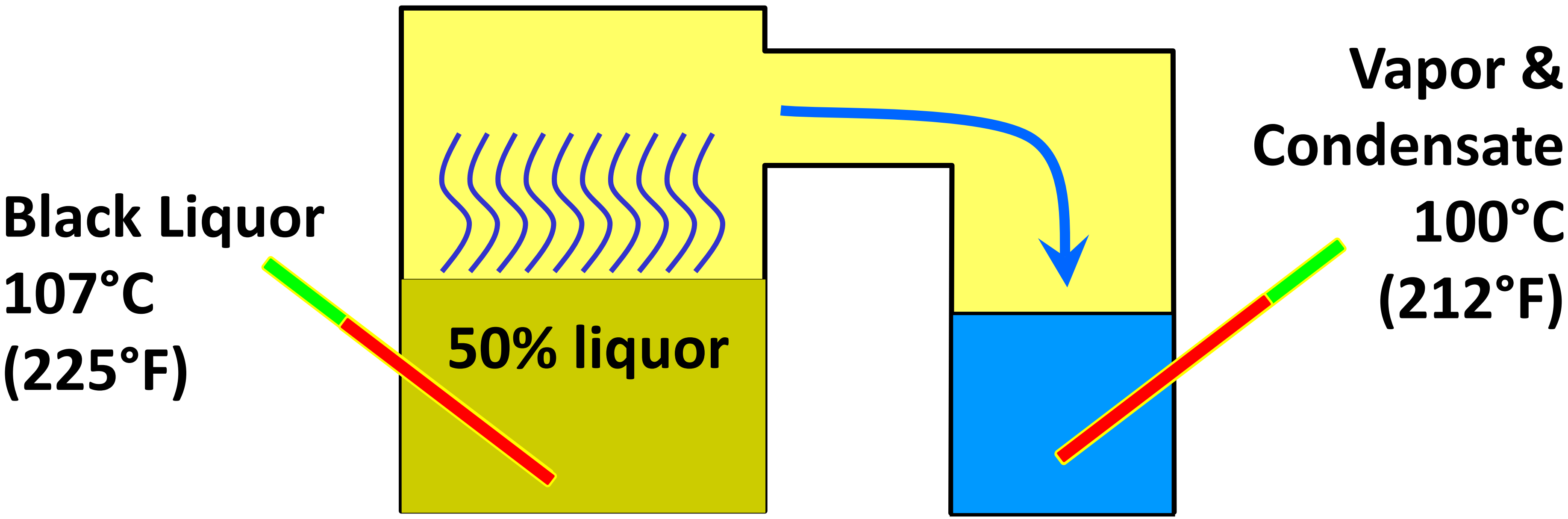
Element/Compound	wt% dry solids
Na	14 - 20
K	0.8 – 5.0
S	3.3 - 6.7
CO_3	2.7 – 8.2
SO_4	1.3 – 10.9
Cl	0.1 – 1.3
C_2O_4	0.2 – 1.3

What Happens During Evaporation?

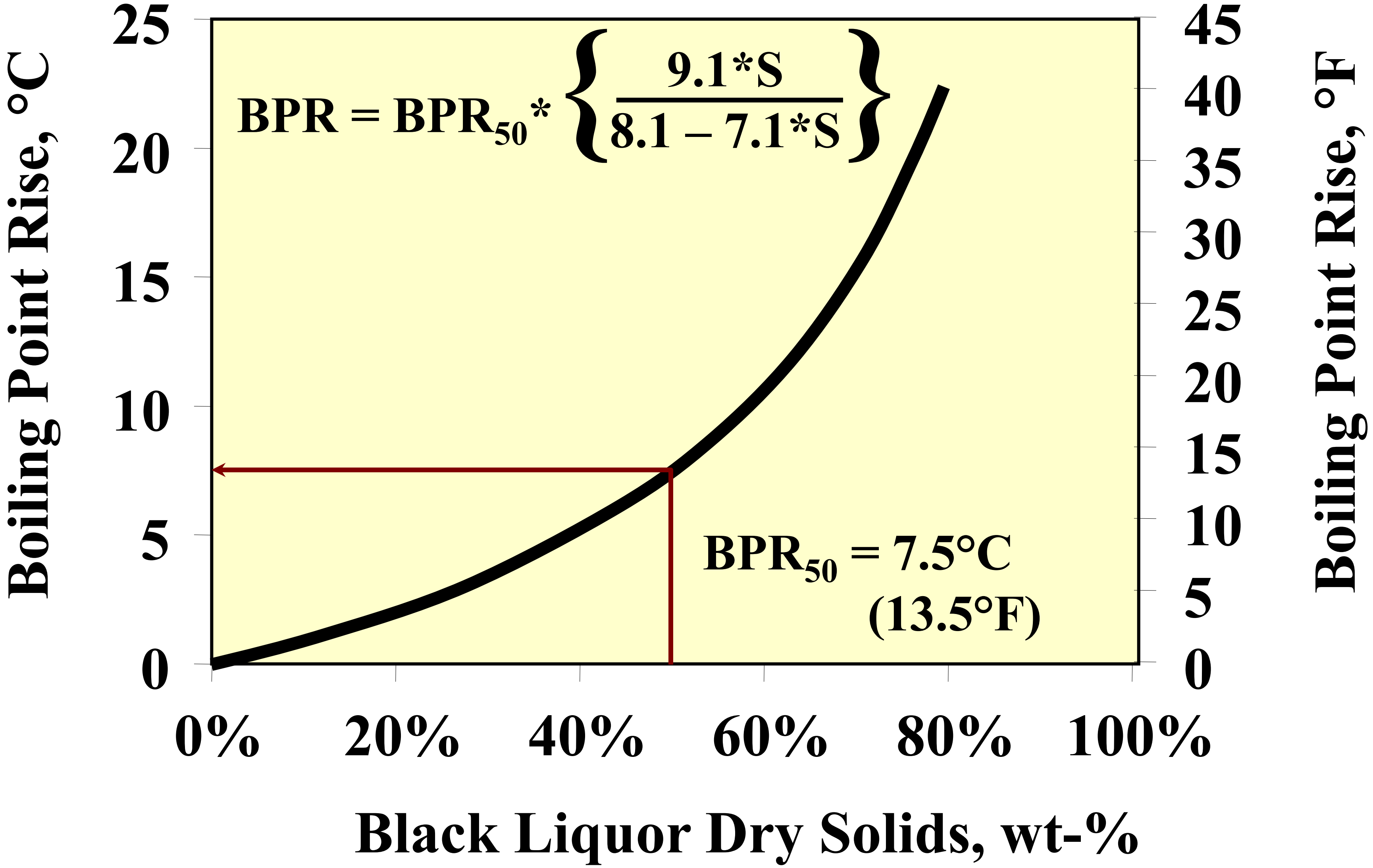


Black Liquor Boiling Point Rise

- Black liquor boils at temperatures above water boiling point



Boiling Point Rise vs. Solids



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

Viscosity

- **Fluid viscosity indicates the magnitude of internal friction**
  - **Corresponds to the informal concept of "thickness": for example, syrup has a higher viscosity than water**
- **Viscosity Impacts**
  - **Heat transfer (*decreases with increasing viscosity*)**
  - **Power usage in recirculation pumps**
  - **Pumpability problems at very high viscosities (high solids and low temperature black liquor)**

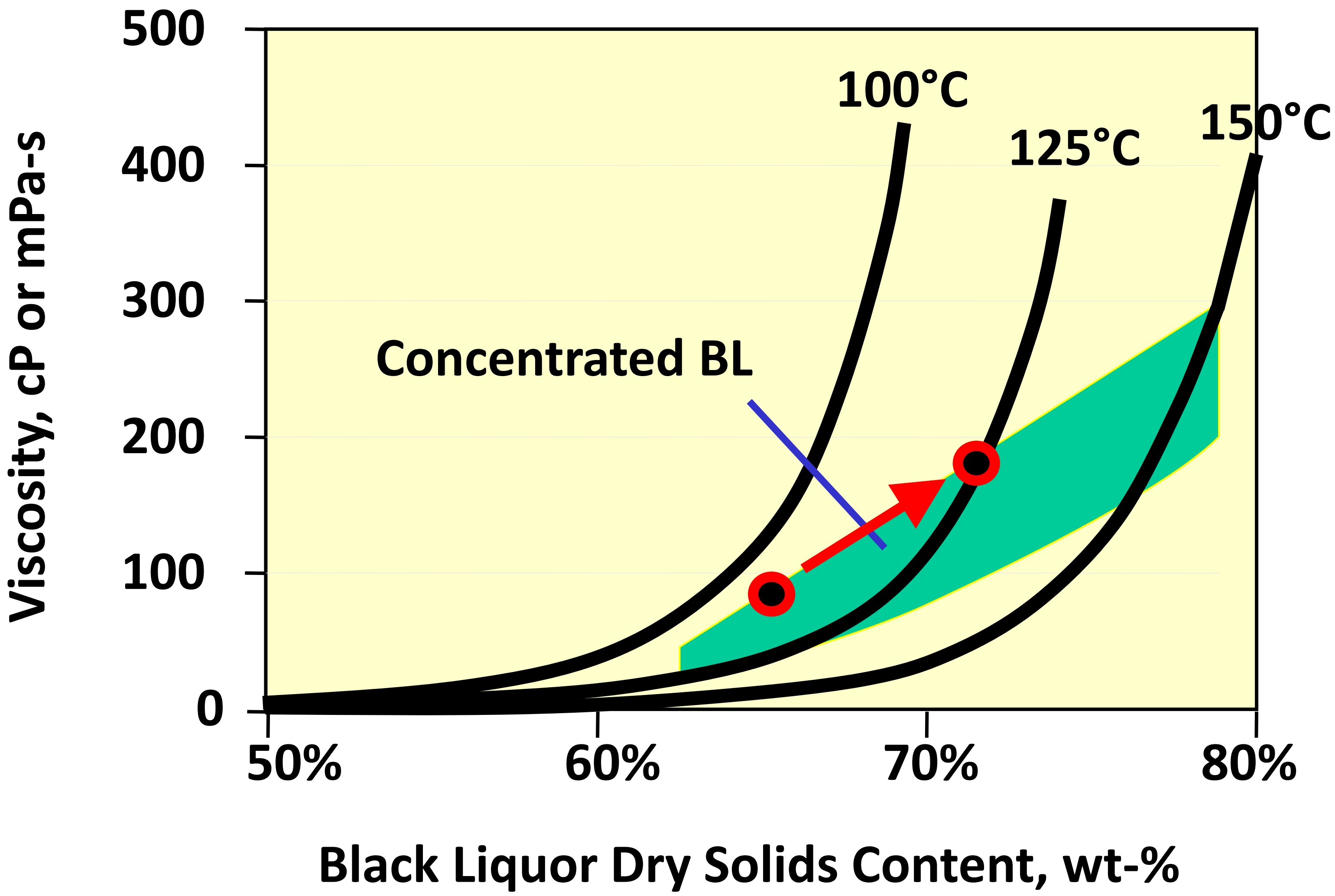
➢ ***Viscosity important for design***

What Determines BL Viscosity?

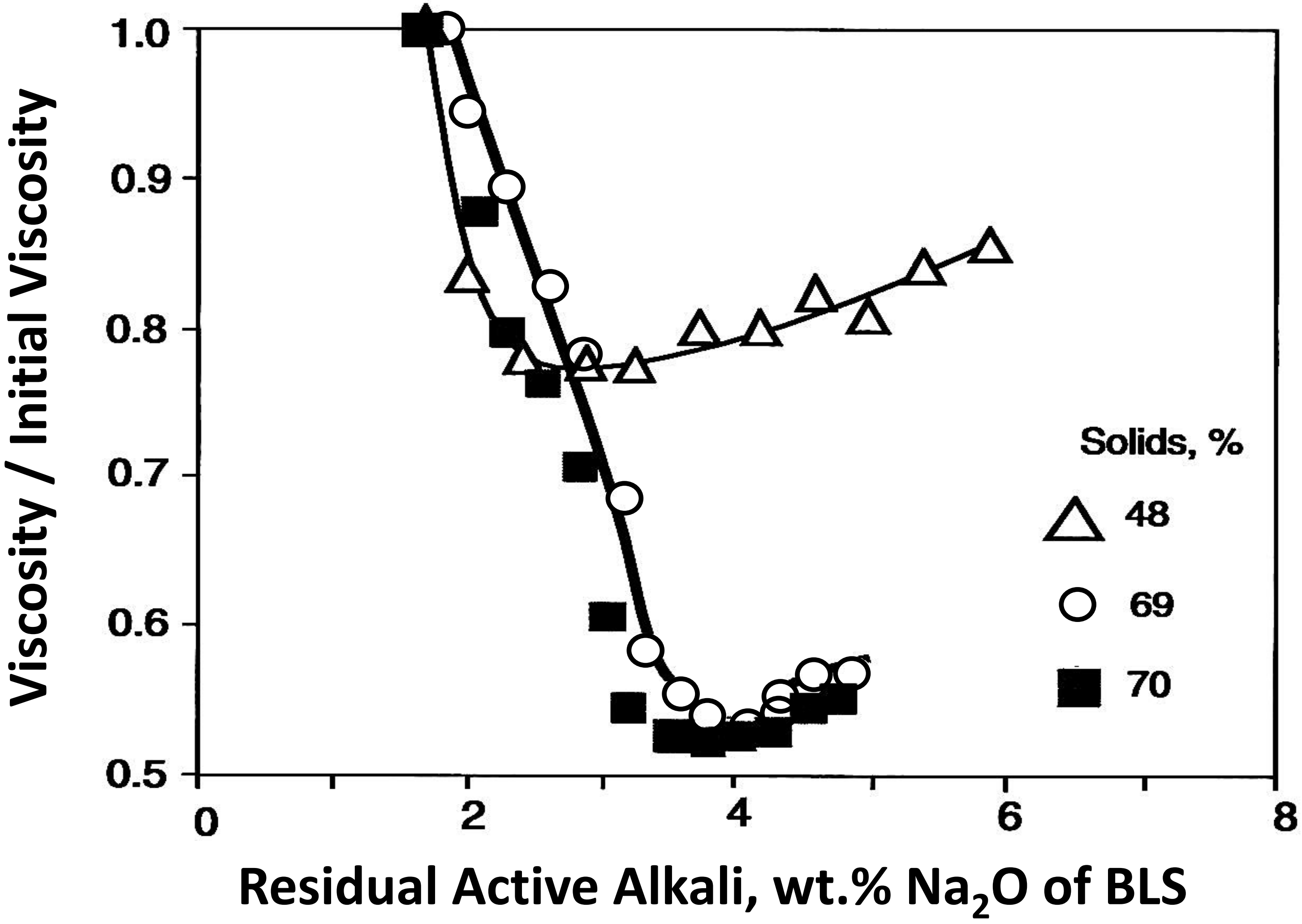
- Dry solids content
- Temperature
- Wood species
- Cooking conditions
- Residual alkali
- Moon phase ☺

- Ideally measured at operating conditions

Black Liquor Viscosity



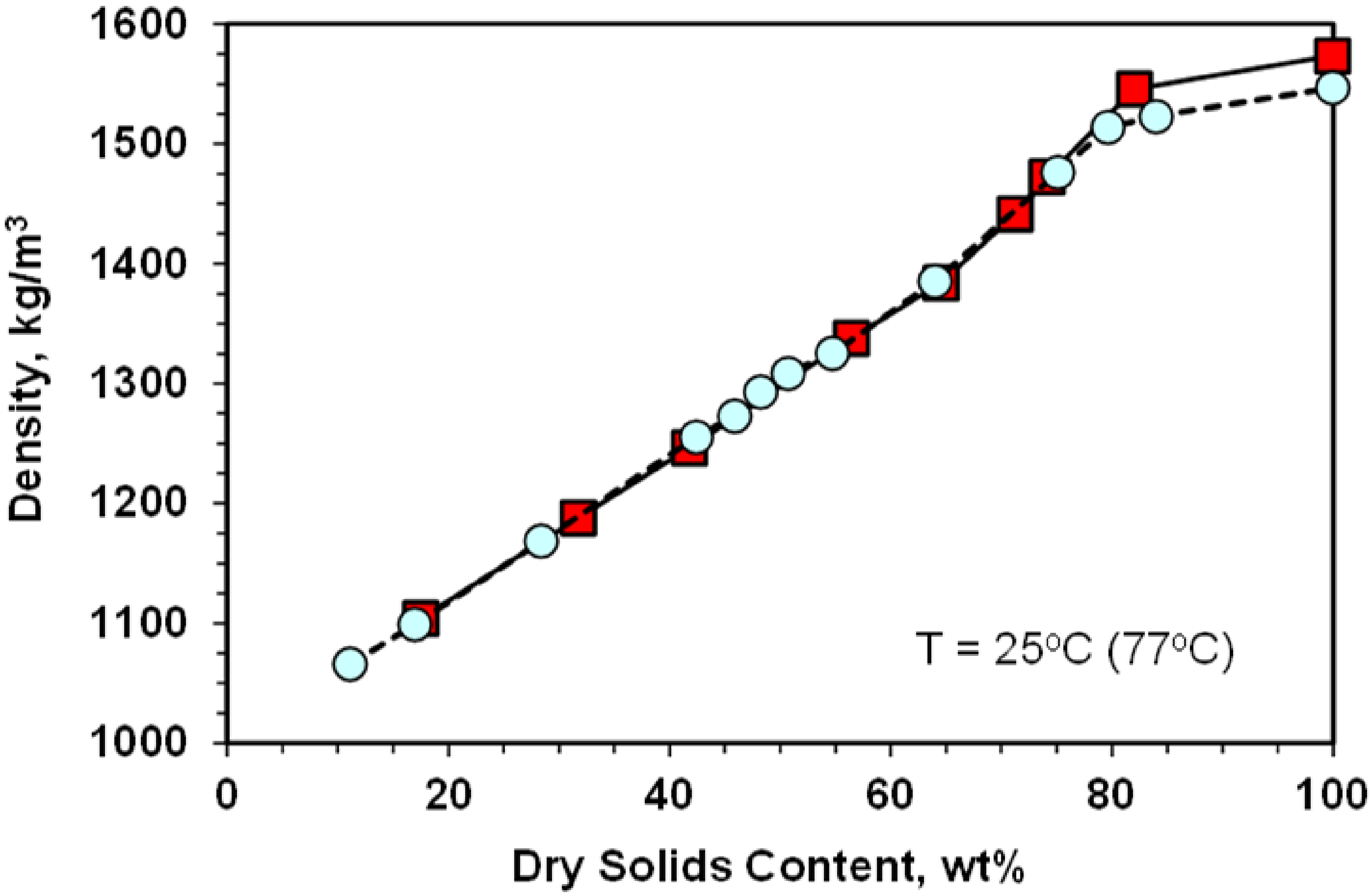
Viscosity vs. Residual Alkali



Milanova, E. and Doris, G.M., J. Pulp & Paper Sci., 16 (3), J94-101 (1990)

Black Liquor Density at 25 °C

- Affects black liquor mass flow rate calculation



Frederick, W.J., Kraft Recovery Boilers – Chapter 3 (2019)

Black Liquor Density

- **Can be approximated using equations below:**

$$\rho_{25} = 997 + 649\ S$$

ρ_{25} = black liquor density at 25°C, kg/m^3

S = black liquor dry solids mass fraction

$$\frac{\rho_T}{\rho_{25}} = 1 - 3.69 \times 10^{-4}(T - 25) - 1.94 \times 10^{-6}(T - 25)^2$$

ρ_T = black liquor density at temperature T, kg/m^3

T = temperature, °C

Frederick, W.J., Kraft Recovery Boilers – Chapter 3 (2019)

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)

- Solids content inferred from ºBaumé
  - useful during boilouts and re-starts
  - correlation changes with wood species!

"Good" Liquor

- Recovery operations is often the culprit for black liquor causing operational problems at evaporators
- Recovery Boiler Reduction Efficiency
  - High is better, greater than 95% should be targeted
- Causticizing Efficiency
  - High is better, 78 to 80% often a good target
- Fiber Content
  - < 40 mg/l
  - Beware of TSS (total suspended solids)

Kraft Liquor Evaporator

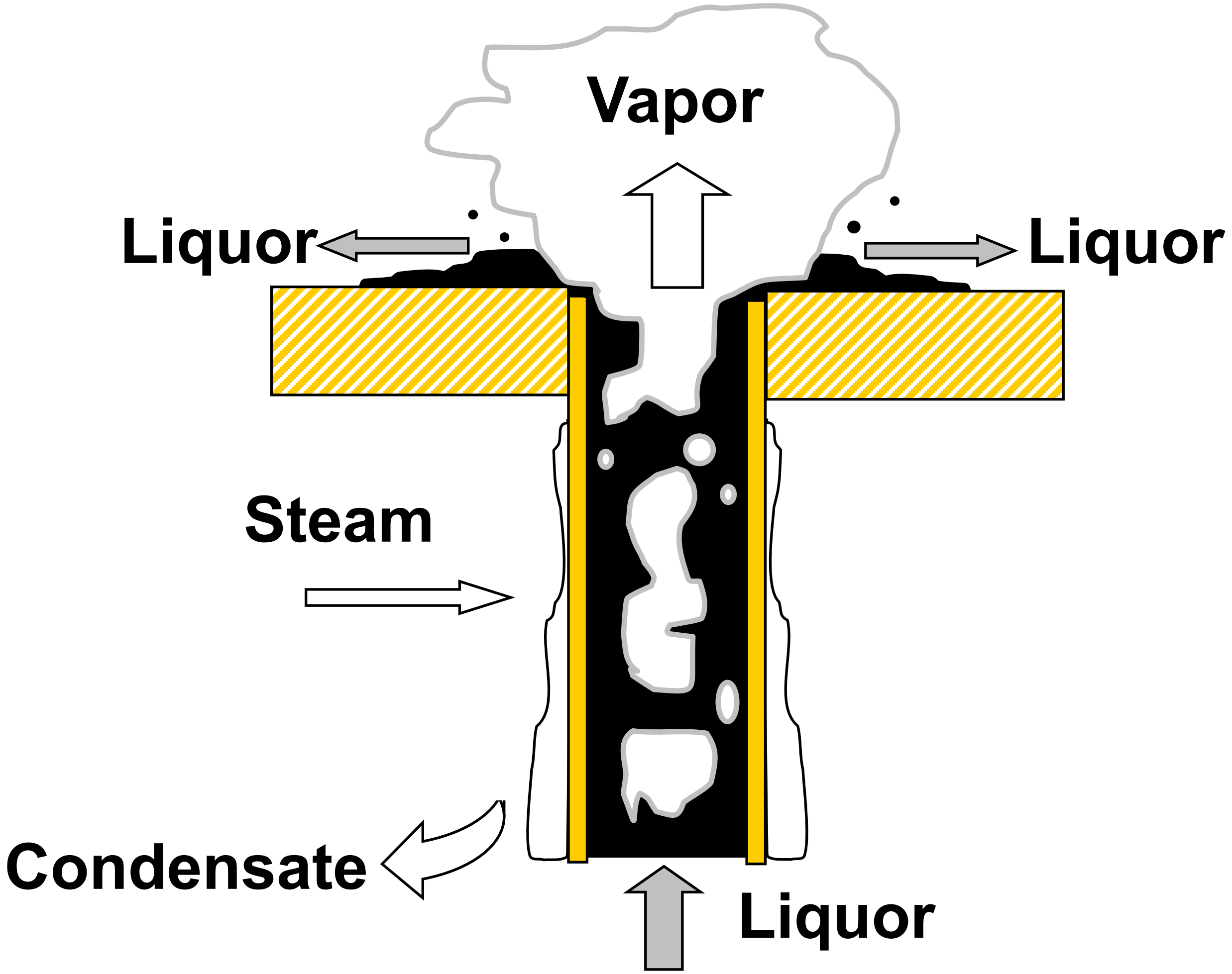
- **Residual (effective) Alkali (as NaOH)**
  - Minimum 2 g/l, ideally 4 to 9 g/l
  - Low -> lignin condensation, fouling
  - High -> Corrosion, loss of capacity

- **Side streams**
  - Neutralize both CTO (crude tall oil) and sesquisulfate to a minimum pH of 10
  - Lower pH causes localized low pH areas -> lignin condensation
  - Return CTO brine after final soap separation

Kraft Liquor Evaporator

- **Primary task**
  - **Concentrate weak black liquor (~15% dry solids content) to firing black liquor (> 65% dry solids content) in a continuous and energy-efficient manner**
- **Secondary tasks**
  - **Produce pure condensate**
  - **Process various side-streams**

Evaporation Basics



Heat Transfer

- **Regardless of type, all kraft black liquor evaporators are governed by**

$$Q = U * A * \Delta T$$

where

Q = Amount of heat transferred (ie. capacity)

U = Heat transfer coefficient

A = Heat transfer area

ΔT = delta-T = temperature difference

= $T_{\text{Saturated steam in}} - T_{\text{Liquor out}}$

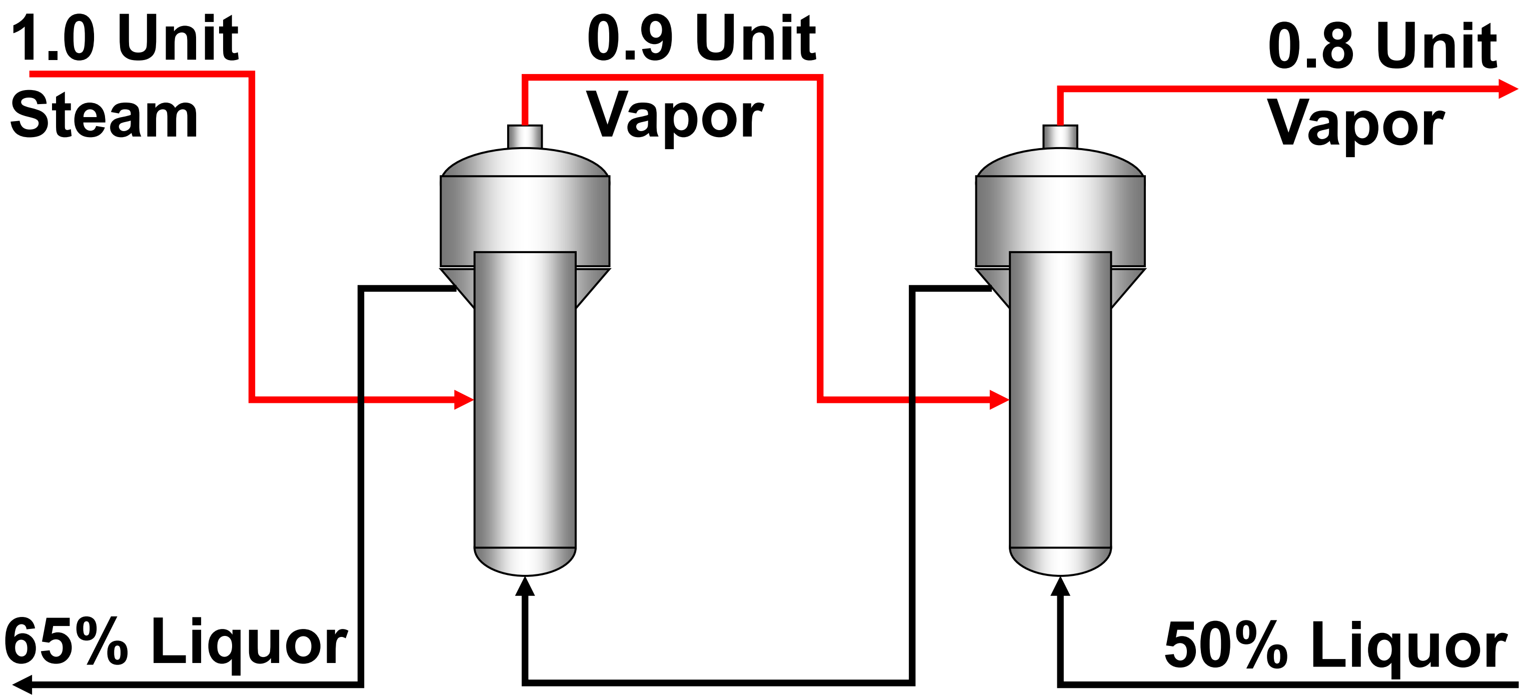
Multiple Effect Evaporation

- In a single-effect evaporator steam is used only once, resulting in steam flow rate to the evaporators that would be more than evaporation rate
- Economic operation requires multiple-effect operation where evaporated vapor from one effect is used as heating steam in the next effect
- Steam Economy is a simple measure of the efficiency of a given evaporator design

$$\textbf{Steam Economy} = \frac{\textbf{Water Evaporated}}{\textbf{Steam Consumed}}$$

- Steam economy can vary from 1.5 to 7

Example: Two-Effect Operation



$$\text{Steam Economy} = \frac{\text{water evaporated}}{\text{steam consumed}} = \frac{(0.9+0.8)}{1} = 1.61$$

Multiple Effect Limits

- Overall ΔT is limited by steam saturation temperature and achievable vacuum
- Example from a recent 7-effect system producing 75% product liquor dry solids:
  - T_{sat} 50 psig (4.5 bar) 298°F (148°C)
  - T_{sat} 26" Hg vac (0.13 bar) 125°F (52°C)
  - ΔT Available 173°F (96°C)
- For modern 7-effect evaporators, roughly 50% of the ΔT available is consumed by Boiling Point Rise (BPR) and pressure losses in the ducting, leaving only an average of 12°F (7°C) ΔT for each effect

Multiple Effect Limits

- ΔT across each effect further decreases as the number of effects increases
  - Only one 8-effect black liquor evaporator exists in North America
- Increasing number of effects from modern “standard” of seven is not considered to be an economically viable alternative to reduce steam consumption
  - There are more economical options for reducing evaporator energy consumption
    - Vapor compression evaporation, systems integration

BPR Example fo 6-Effect LTVs

Effect #	BL Dry Solids	BPR, °C	BPR, °F
6	18%	1.8	3.2
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Total		24.3	43.7

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

Ex. ΔT = 298 °F – 125 °F – 44 °F = 129 °F

Evaporator Types

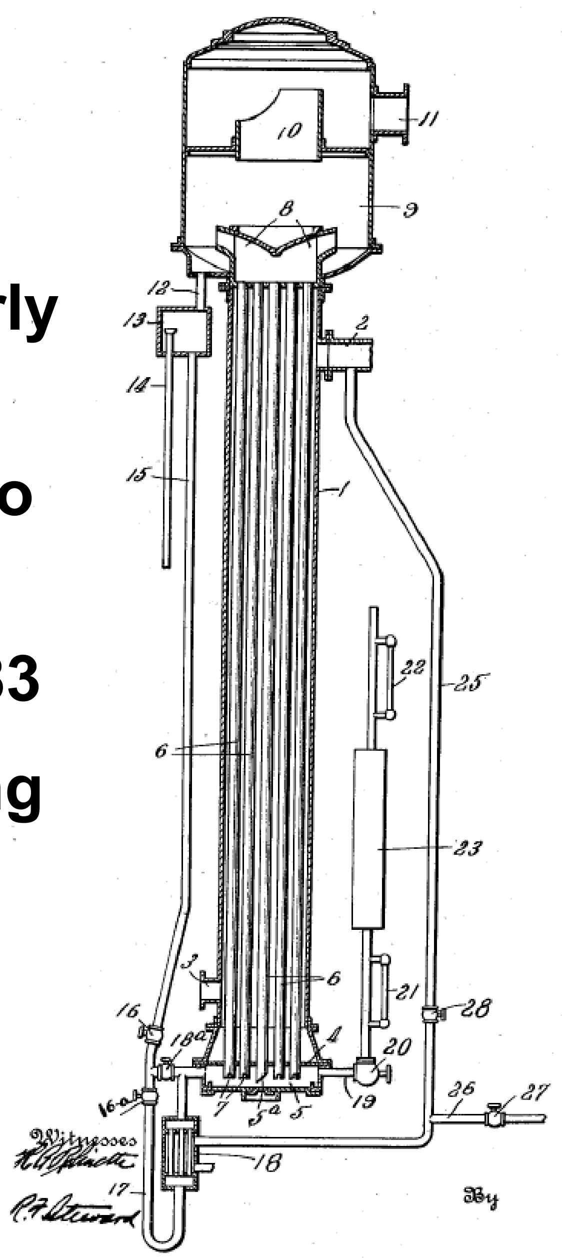
- **Long Tube Vertical (LTV)**
  - **Rising-film type evaporator utilizing mostly tube-type heating surface**
  - **Liquor movement upwards inside tubes**
    - **Movement caused by heating and action of water vapor generated by boiling**
  - **Obsolete by modern standards but still in use in many North American mills**

Evaporator Types

- **Forced Circulation (FC)**
  - **Forced circulation type evaporator utilizing mostly tube-type heating surface fully submerged in liquor**
  - **Liquor movement caused by circulation pump**
  - **Originally used for high solids units**
  - **High power consumption has reduced its use in modern mills**
- **Falling Film (FF)**
  - **Utilizing various heating surface types**
  - **Liquor falls over the heating surface by gravity**
  - **Current standard technology for new evaporators and concentrators**

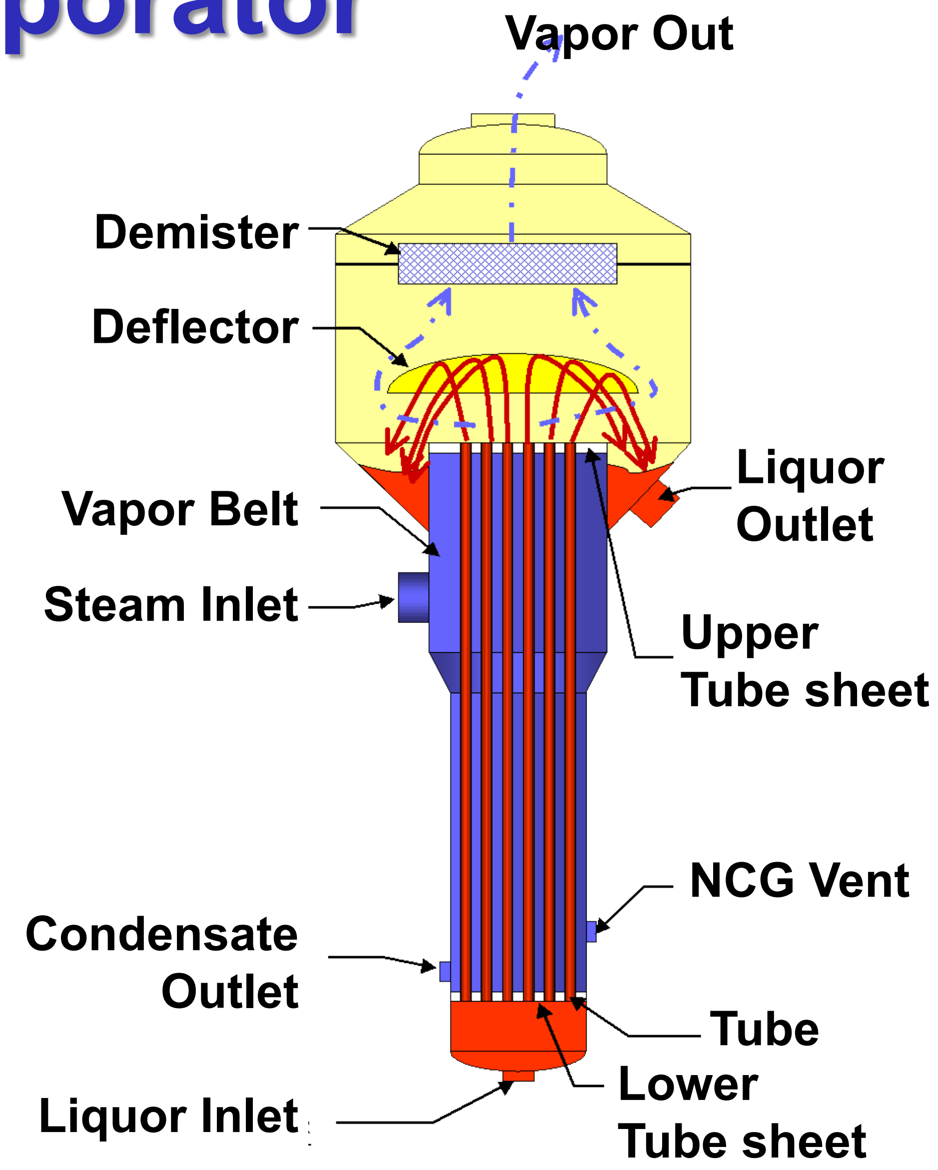
LTV Evaporator

- Oldest black liquor evaporator
- Many designs are by Paul Kestner in early 1900's
- Still a workhorse in North America due to large installed base
- Last LTV evaporator set delivered in 1983
- No circulation pump - Minimum operating costs
- Can be operated with minimum instrumentation

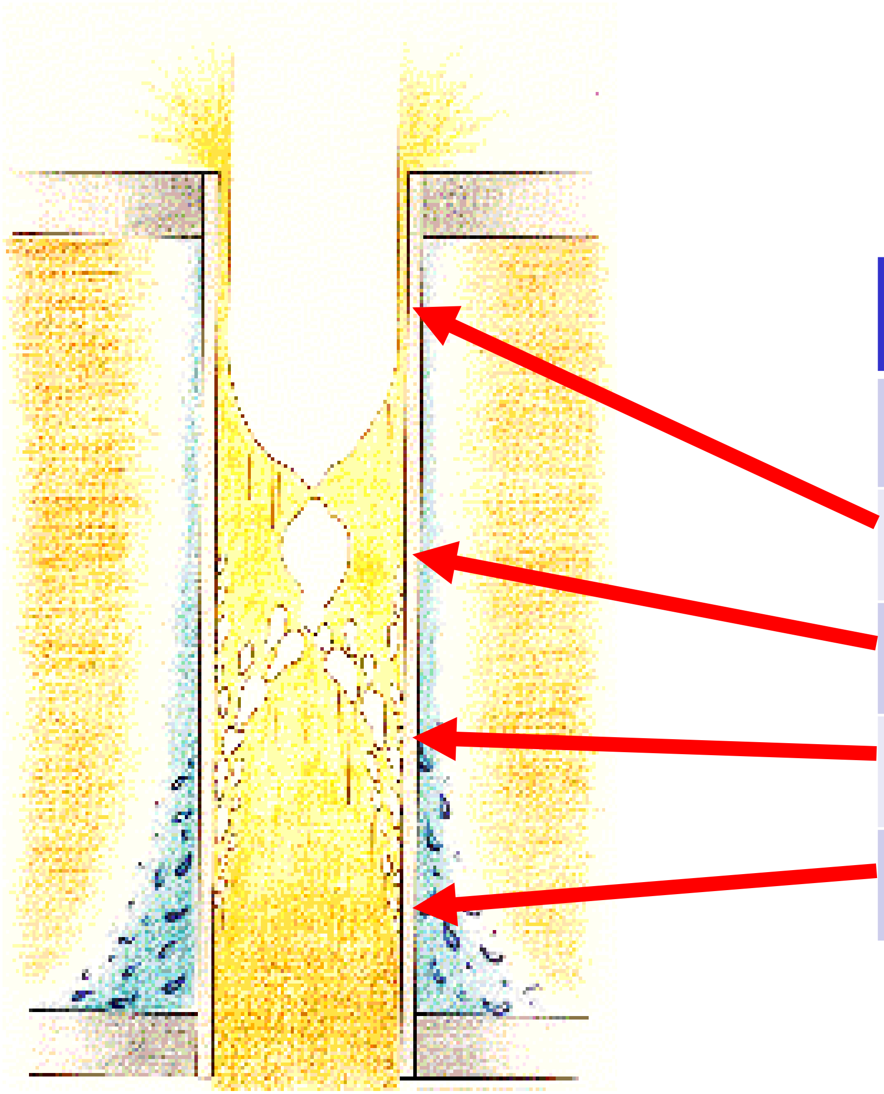


LTV Evaporator

- Liquor enters the tubes from the bottom
- Liquor film moving upwards is created by vapor formed by boiling liquor at the bottom of the tubes
- Liquor film formation requires sufficiently high load (high ΔT)
  - Limits LTV use for practical maximum of 6 effects
  - Limits LTV turndown capability



LTV Evaporator Regions



Boiling Type	U
Stripped Film	Very Poor
Film Boiling	Excellent
Bulk Boiling	Good
Bubble Boiling	Good
Pre-heating	Poor

FC Evaporator

- Large liquor volume is circulated through a submerged heater
- Heated liquor flashed in adjacent flash tank
- For black liquor most common use as “concentrator” for 50% or above liquor
- Circulation pump power consumption became a drawback

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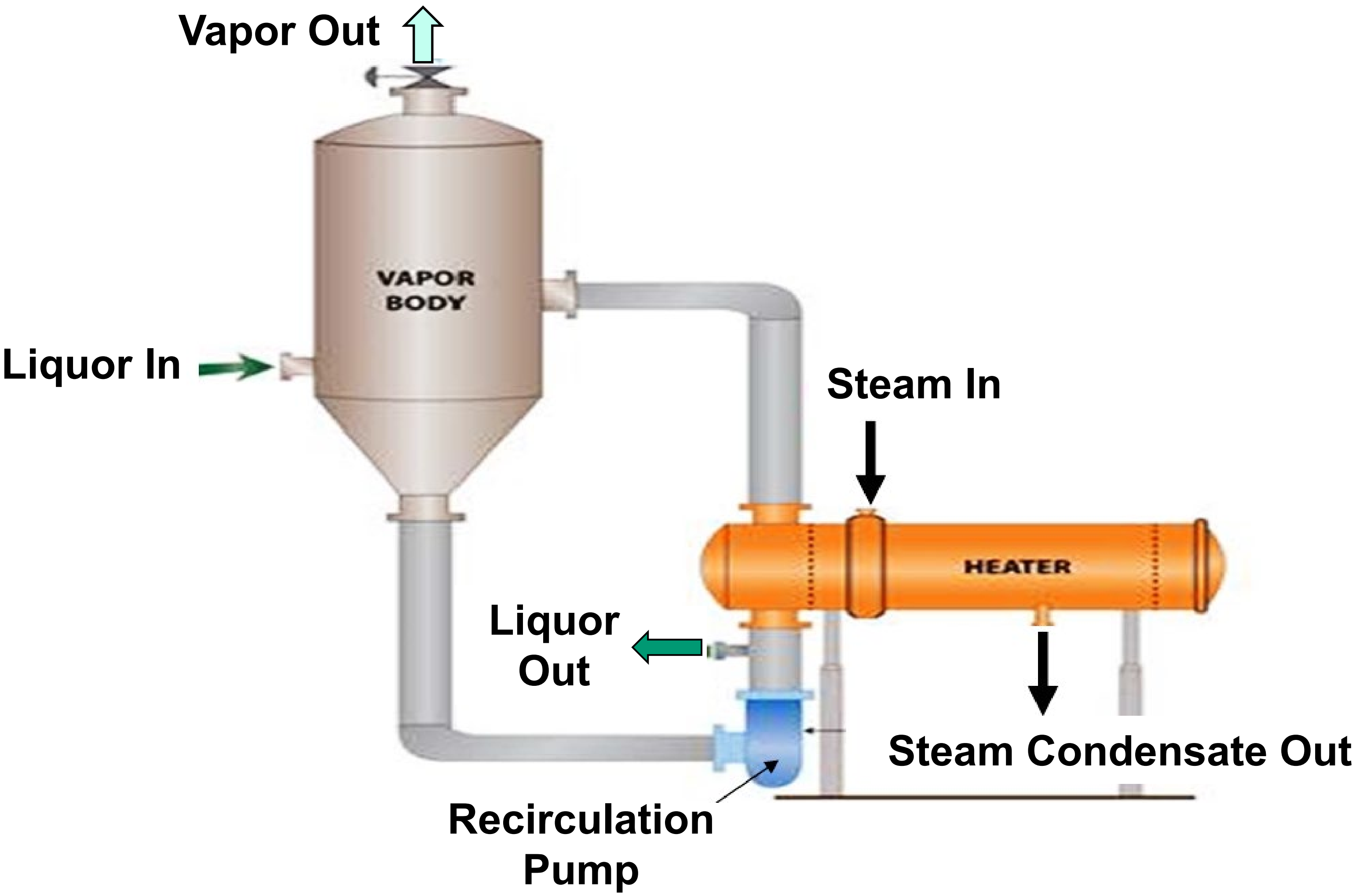
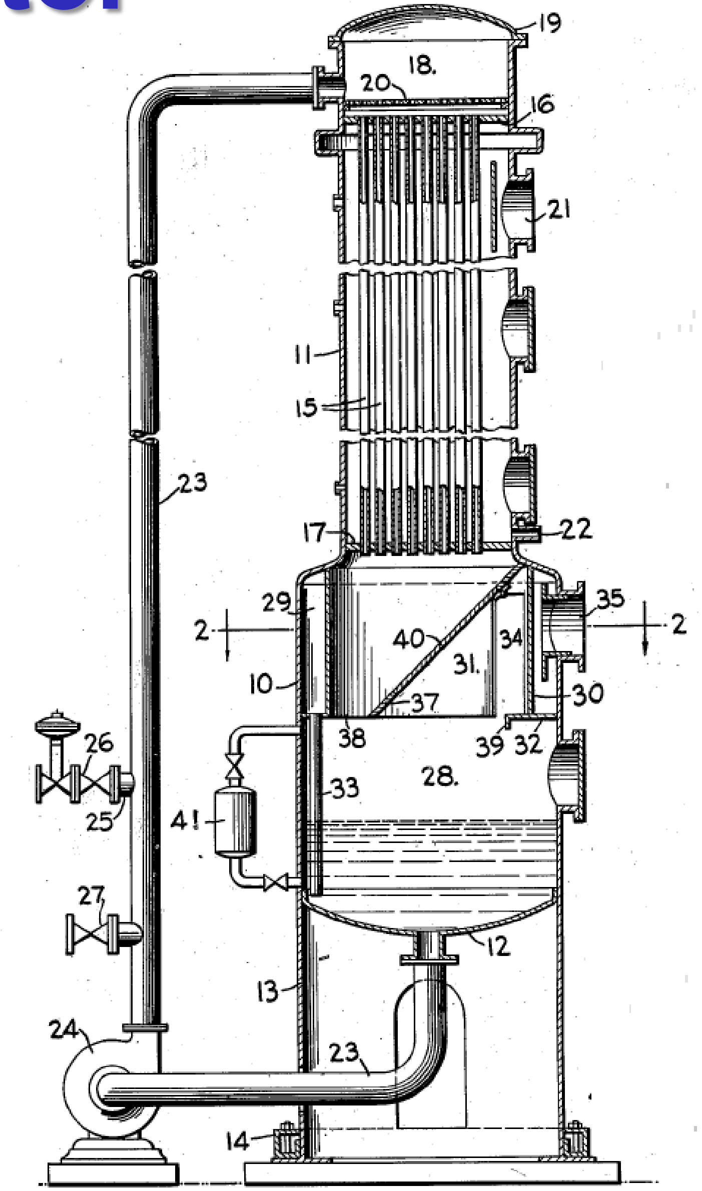
FC Evaporator



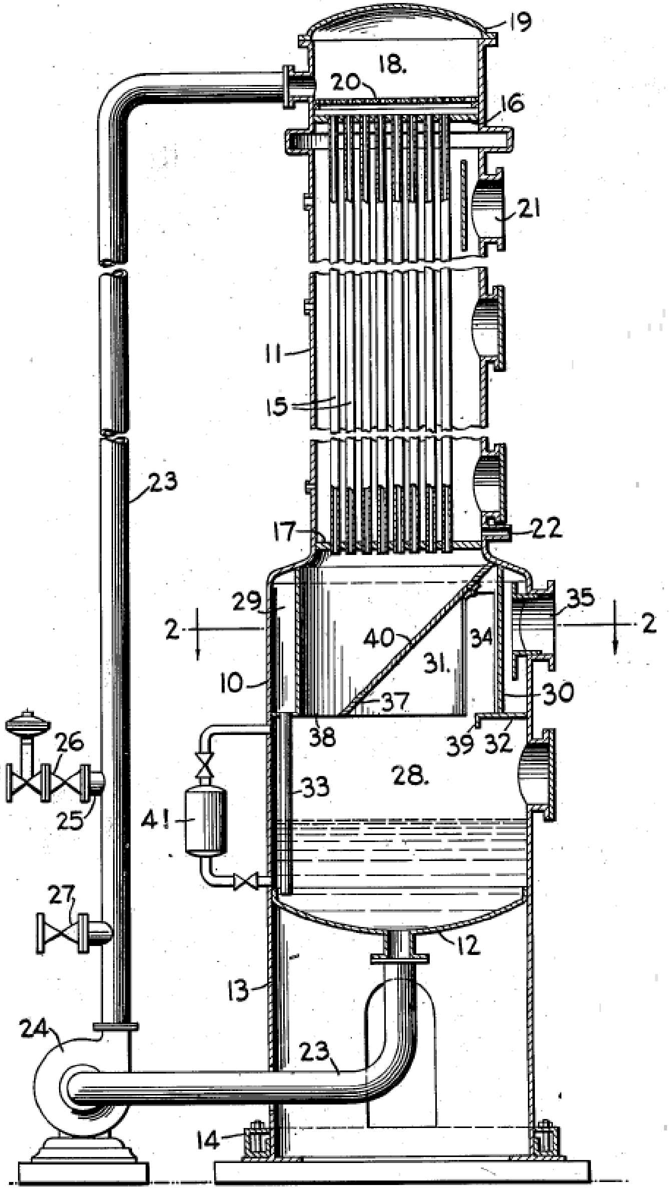
FF Evaporator

- Original design by Zaremba Company
  - Patent drawing from 1949 shown but there were earlier designs
- Became established in the Pulp and Paper industry in the 1980's
  - First single units already in the 1930's/1940's

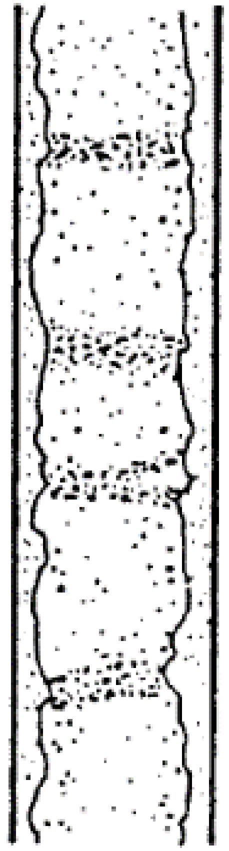


FF Evaporator

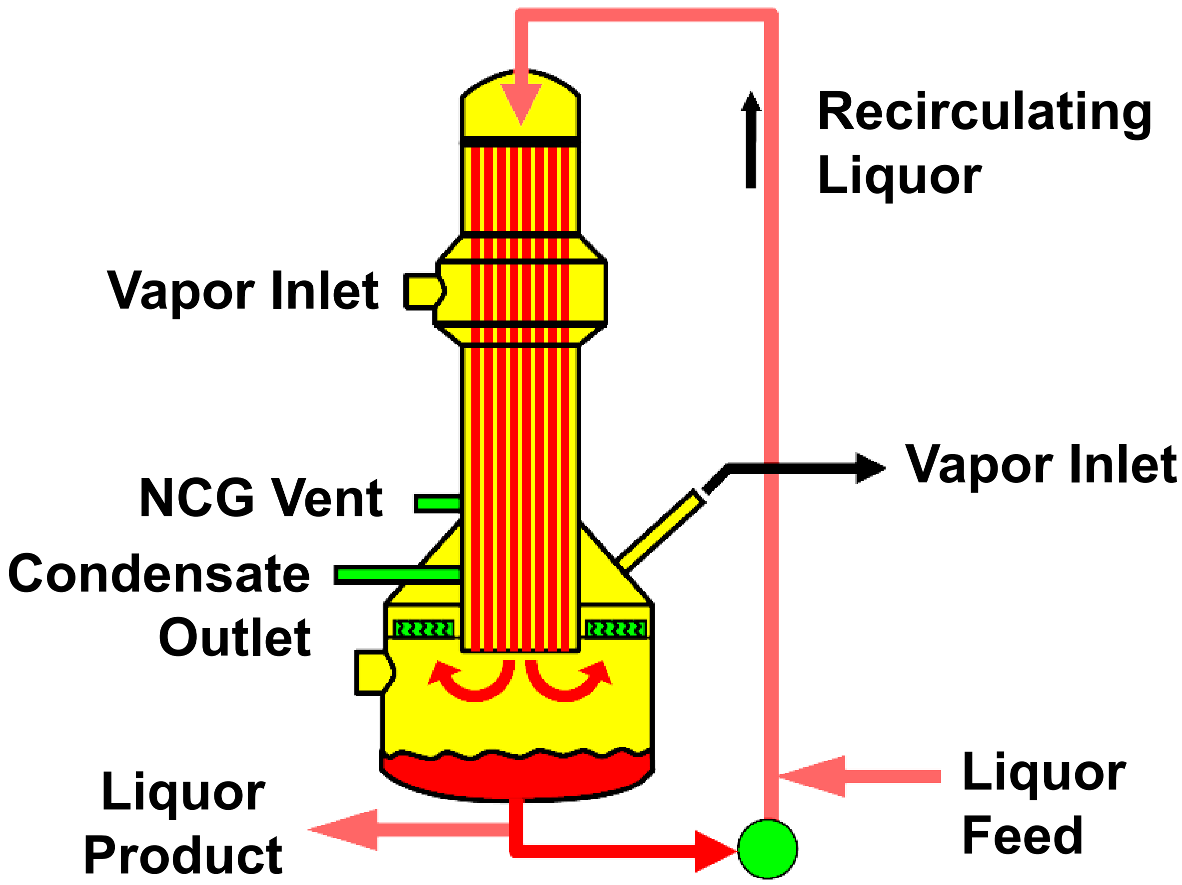
- Nowadays the standard for modern black liquor evaporator sets
- Modest liquor circulating pump and distribution system provides even liquor film regardless of the load or operating conditions



Tubular FF Evaporator



FALLING FILM
(Annular flow)



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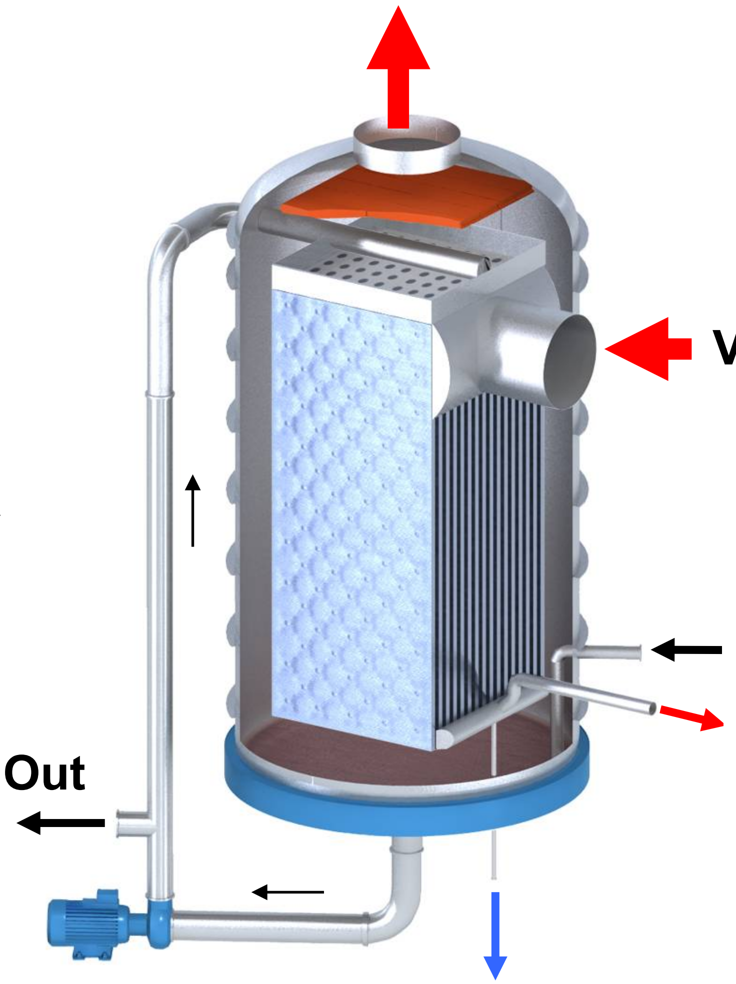
Lamella (Plate) FF Evaporator

- Heating surface is made from pillow-plate shape heating elements
- Steam/vapor condenses on the inside, falling liquor film on the outside
- Liquor is circulated with a circulation pump and distributed on top of the heating surface



Tubel® FF Evaporator

- Same design concept as plate type evaporators but with tubes
  - Liquor on the outside, steam on the inside
- Typically multiple bodies where one body can always be put on wash

Evaporator Type Selection

- All three types are in common use in the industry
- Modern mill requirements:
  - Single line → High turndown, reliable operation
  - Minimum operating costs
  - High steam economy → Maximum number of effects
  - Low pump electric power consumption
  - Optimum condensate quality
- These requirements have converged modern new evaporators into a design using falling film technology with 7 or 7 ½ thermal effects and multiple 1st effect (“concentrator”) bodies

Evaporator Operation

- Primary objective is to have sufficient capacity to meet pulp mill and recovery boiler demands
- Once this is met, typical second objective is operating cost minimization
- All effects and auxiliaries must perform for maximum capacity to be realized
- Liquor side fouling control, mitigation and fouling removal (normally by a boil-out) are part of day-to-day operations for most units
- Common other operational issues are discussed later in evaporator troubleshooting

Challenges for Materials of Construction

- Inorganic salts in black liquor increase in corrosivity as temperature and liquor solids increase throughout the evaporators and concentrators
- Especial concern is Stress Corrosion Cracking (SCC) of austenitic stainless steels caused by NaOH and Na_2S at elevated temperatures

Materials Selection

- Traditional selection until 1990's was mixed construction
  - Mixed carbon steel and 304-grade stainless steel for weaker effects, all 304-grade stainless steel for stronger effects
  - Many still in operation today
- Increase in final dry solids and other changes have changed modern selection to
  - All 304-grade (304L) stainless steel for weaker effects
  - Duplex stainless steel grades (S32101, S32304, S32205) for concentrators
    - To eliminate risk of SCC