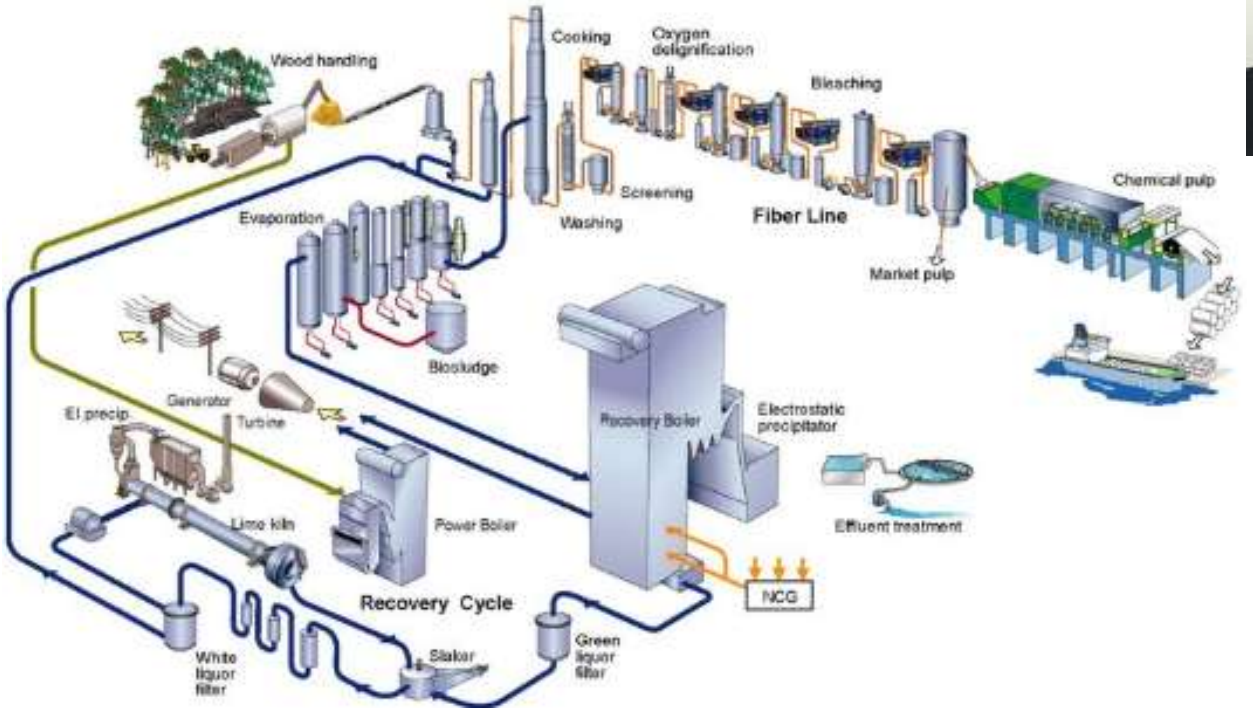
ENMAS ANDRITZ

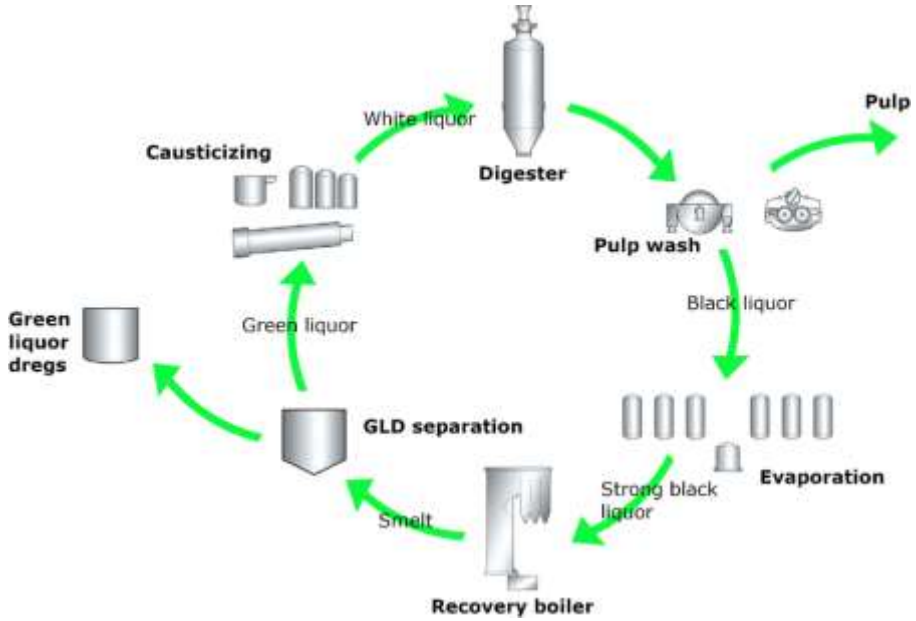
BASICS OF CHEMICAL RECOVERY – PULP & PAPER

R Chandrasekaran 04.06.2025



CHEMICAL RECOVERY MISSION

- The three purposes of recovery systems are:
  - **Environmental impact mitigation**, by treating and disposing of waste liquor (black liquor) from pulping Production of steam for turbine and process
  - **Chemical recycling**, by recovering pulping chemicals like sodium hydroxide (NaOH) and sodium sulfide (Na2S) for reuse,
  - **Energy generation**, by burning organic matter to produce steam and electricity.

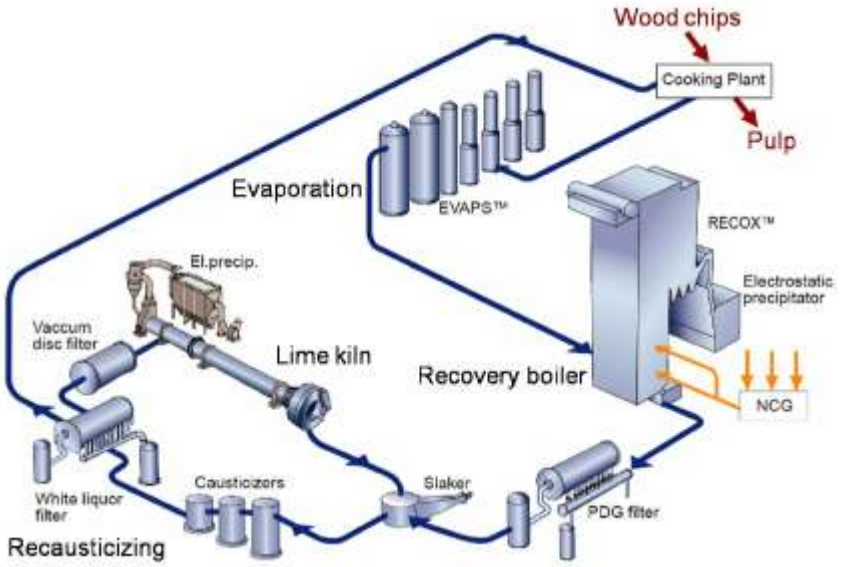


Over all view of Pulp mill

Kraft pulp mill: recovery cycle

The process steps included:

- Evaporation - (from weak black liquor to strong black liquor)
- Recovery boiler (combustion of strong black liquor and reduction sodium sulfate to sodium sulfide)
- Smelt dissolution (Green Liquor production)
- Re-causticization (Reaction of green liquor with calcium oxide to make white liquor and calcium carbonate)
- Lime cycle (burning lime from calcium carbonate to calcium oxide)



CHEMICAL RECOVERY – QUICK UNDERSTANDING

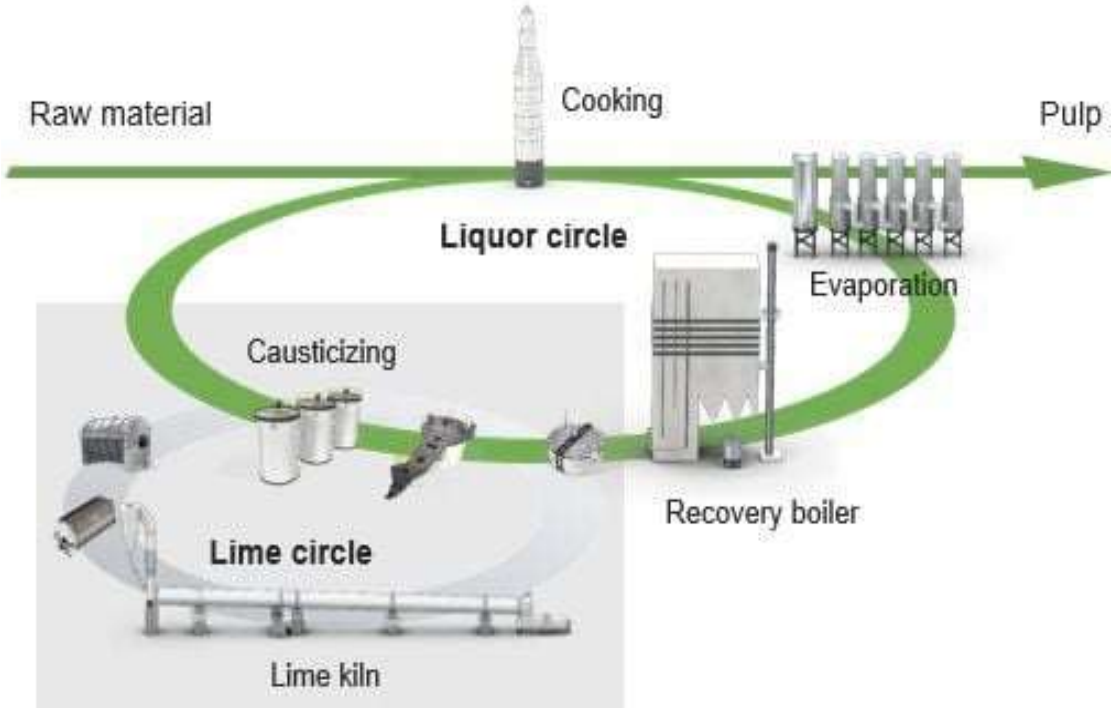
- The 4 process steps 4 C's

➢Concentration – Evaporation

➢Combustion - Recovery boiler

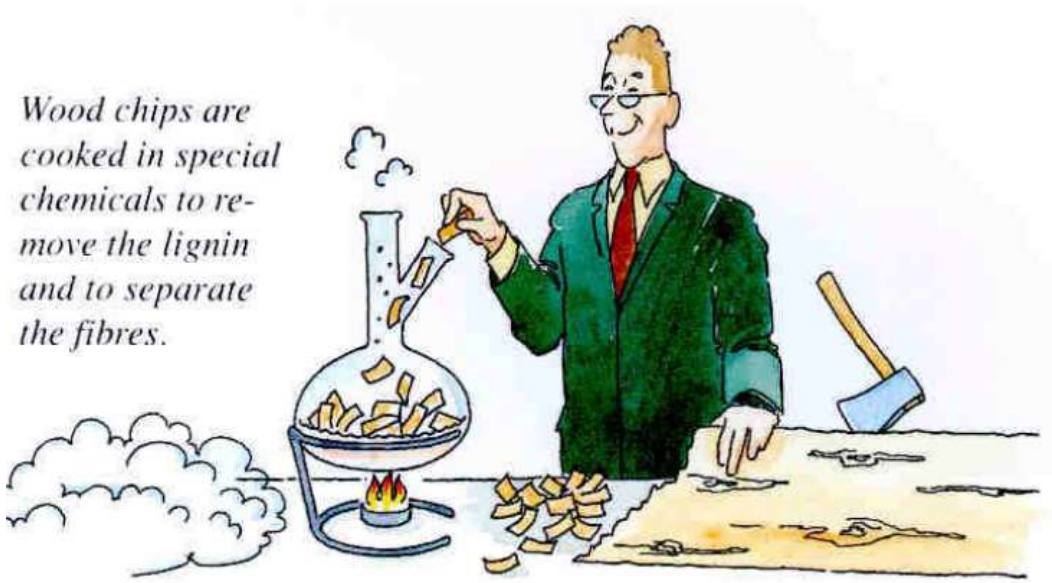
➢Causticization – Re-causticizing

➢Calcination - Lime cycle



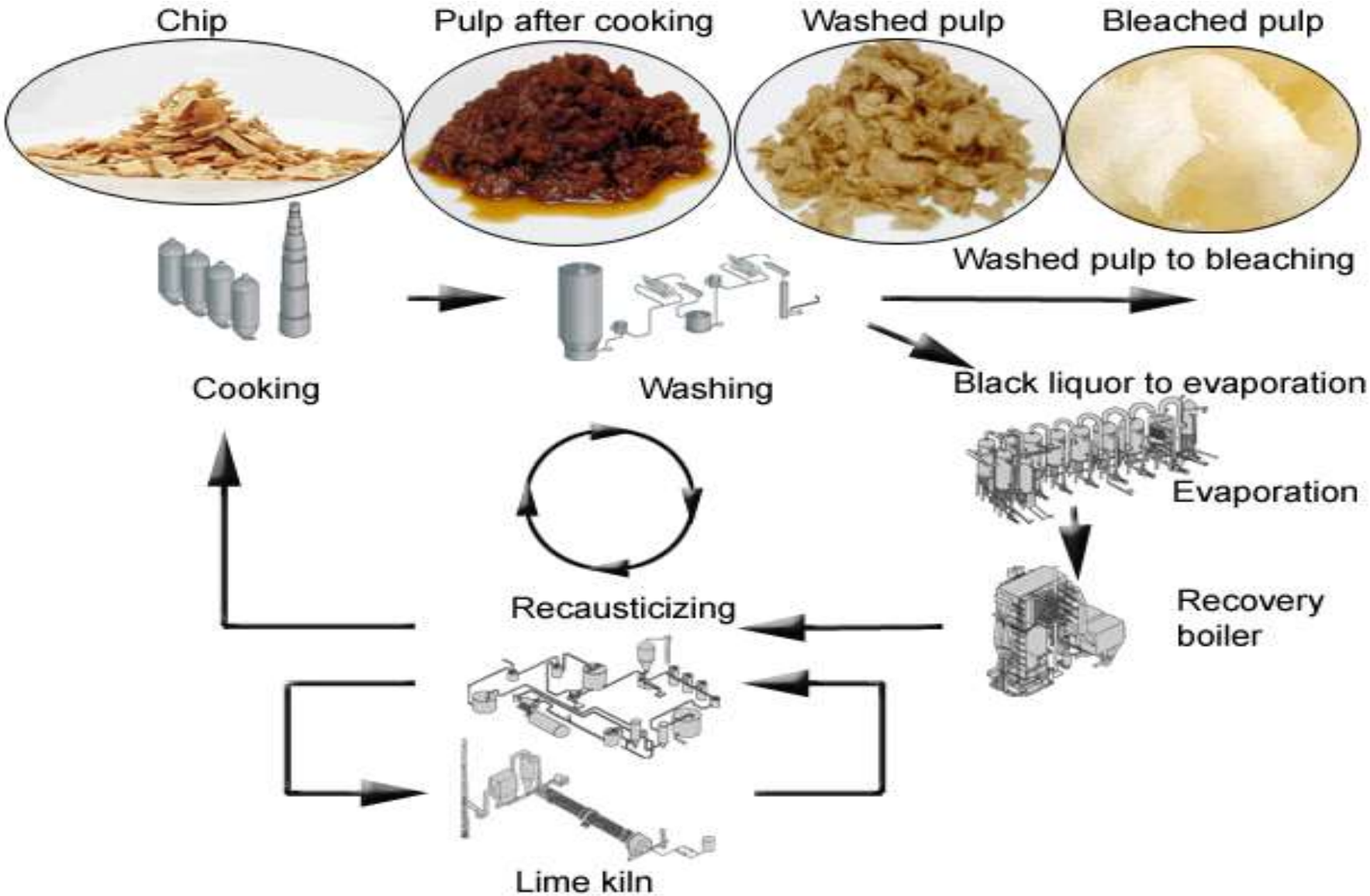
CHEMICAL RECOVERY

- **Black liquor** is the by-product from the kraft process when digesting pulpwood into paper pulp
- Removing lignin, hemicelluloses and other extractives from the wood to free the cellulose fiber



CHEMICAL RECOVERY

CHEMICAL RECOVERY



What's Black Liquor?

- Complex mixture
- Spent pulping chemicals (Inorganic salts, caustic, etc.)
- Organic matter (Lignin) dissolved from the wood
- Non-Process-Elements (NPE) such as K, Cl, etc.
- Brought in with wood, water and fresh chemicals
- No purge points: Constantly recycled

Black Liquor Properties

- Chemical composition
- Major role on the performance of the evaporators
- Na_2SO_4, Na_2CO_3 co-precipitate at high solids
- Risk of scale formation
- Critical physical properties
- Boiling Point Rise (BPR)
- Viscosity which impacts heat transfer

Typical black liquor analysis

Agent	Content [% of dry solids]
Na	19.3
K	3.34
S_{tot}	5.50
Cl_{tot}	0.41
C	31.9
O	36.14
H	3.33
N	0.08
(Compounds, incl. elements above:)	
NaOH	1.1
CO_3^{2-}	6.2
Na_2SO_3	0.1
$Na_2S_2O_3$	2.13
Na_2SO_4	1.23
S^{2-}	1.93
Calorimetric heat value, HHV (MJ/kg dry solids)	12.74

Black Liquor evaporation

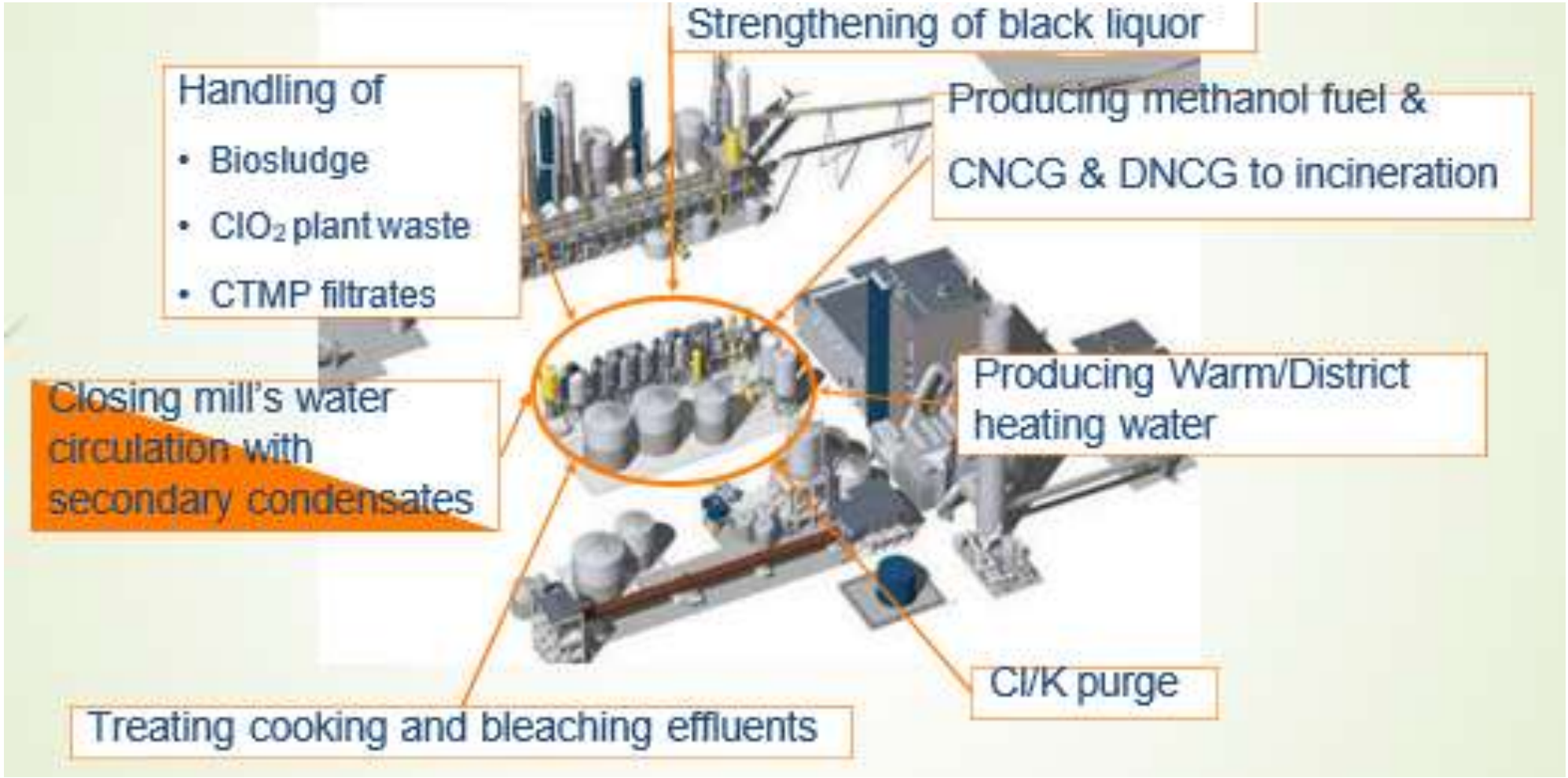
- Black liquor recovered from pulping contains 10-17% dissolved solids
- These solids are composed of about 1/3 inorganic chemicals that were in the white liquor added to the digester
- The remaining 2/3 consist of the organic chemicals extracted from the wood
- Black liquor must be concentrated to above 60% solids so that it will burn without supplemental fuel

Black liquor + Heat → Strong Black liquor + Water + Steam

Condensate + Steam → Clean + Dirty condensate + NCG

Black liquor → Black liquor + Soap (only softwood)

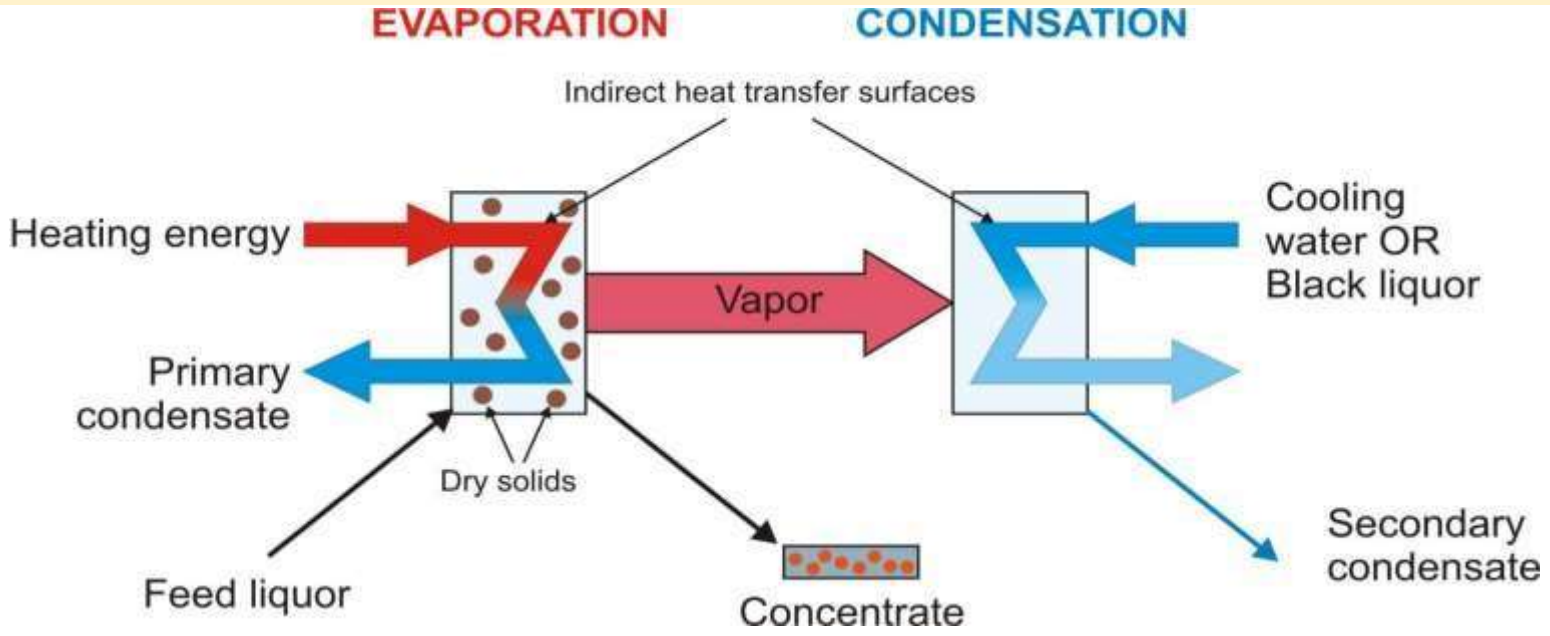
Evaporator Focus on



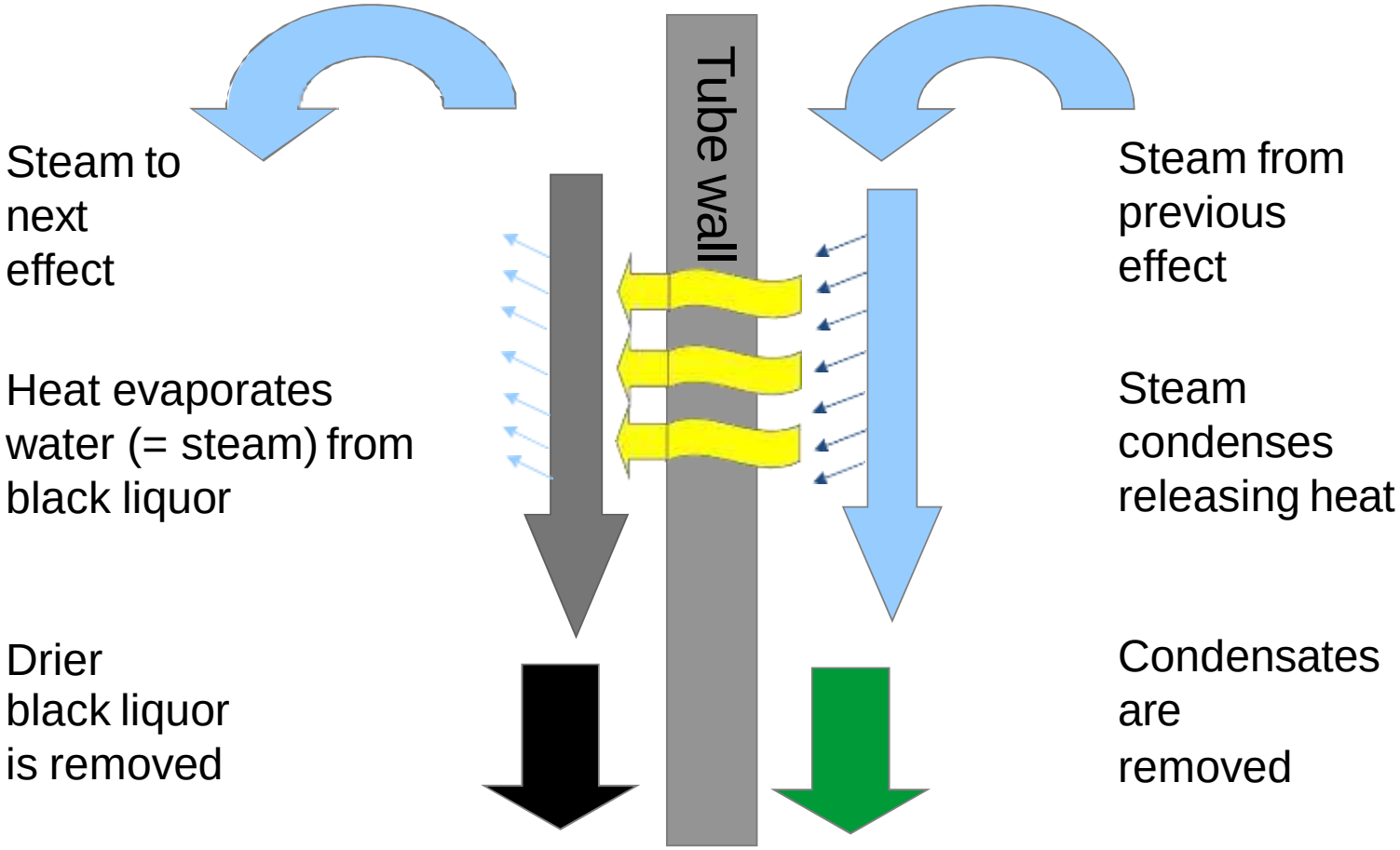
Evaporation capacity

- Typically expressed as ton H_2O/h or kg H_2O/s
- Evaporation capacity is determined by the heating surface area(A), available temperature drop(T) and overall heat transfer coefficients
- Process governed by the heat transfer law

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

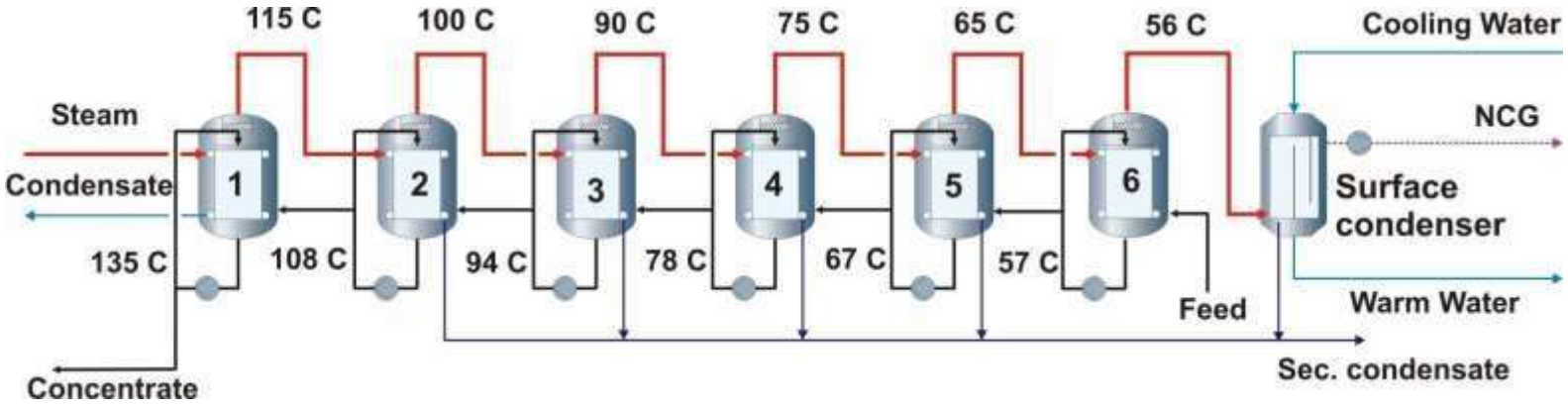


Basics of evaporation



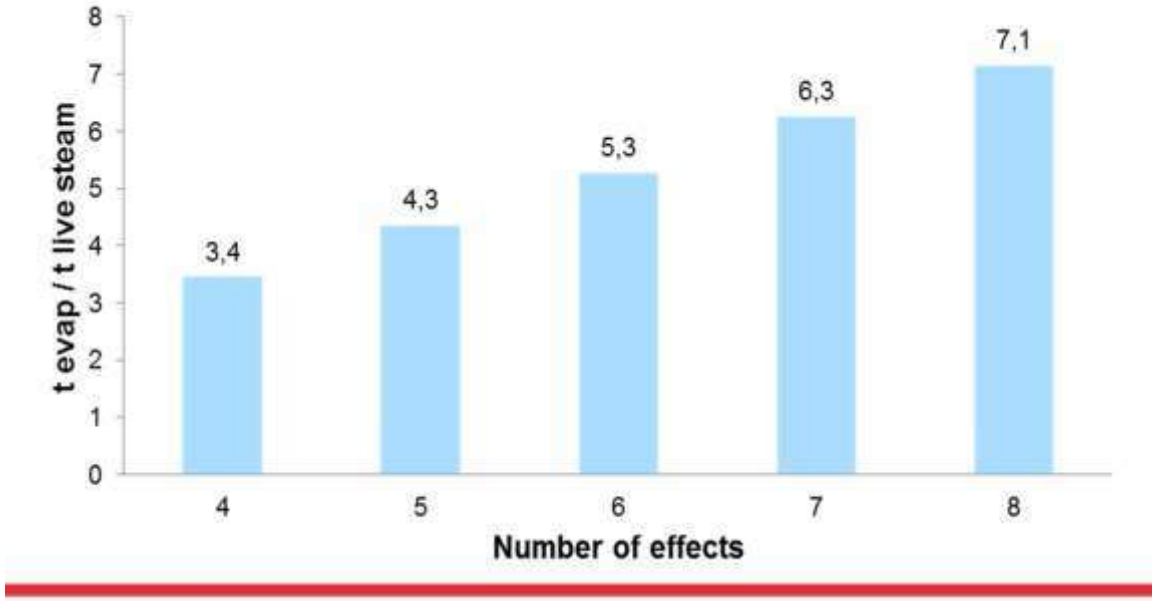
Basics of evaporation

- Multi effect evaporation (MEE), 6-7 effects
  - 1 st effect uses primary LP & MP steam
  - 2-7 effects use secondary vapor
  - last effect vapor is condensed with cooling water in surface condenser
  - evaporation done mainly by secondary vapor

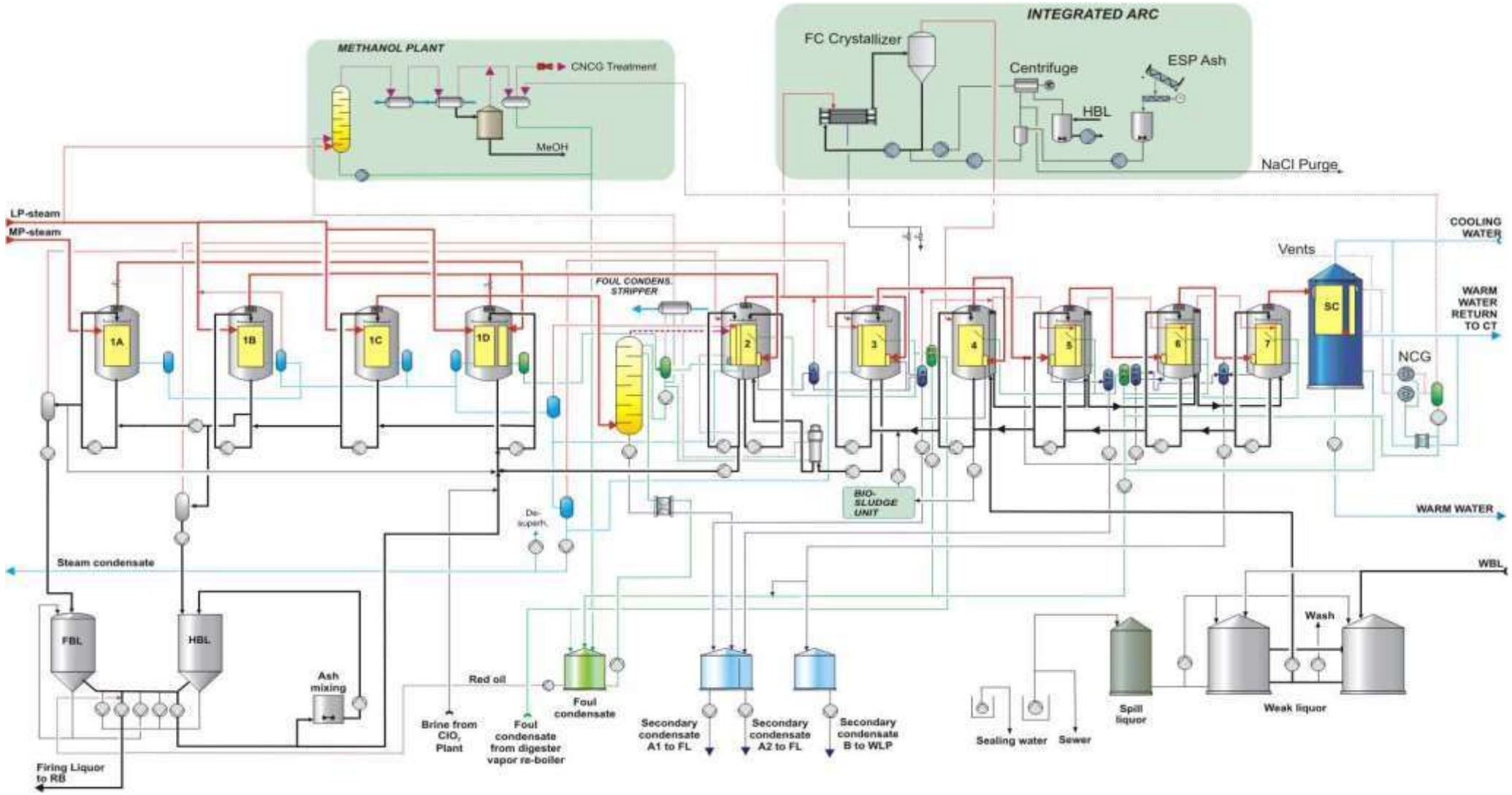


Basics of evaporation

- The more effects the better is the steam economy
- But the higher is the equipment cost

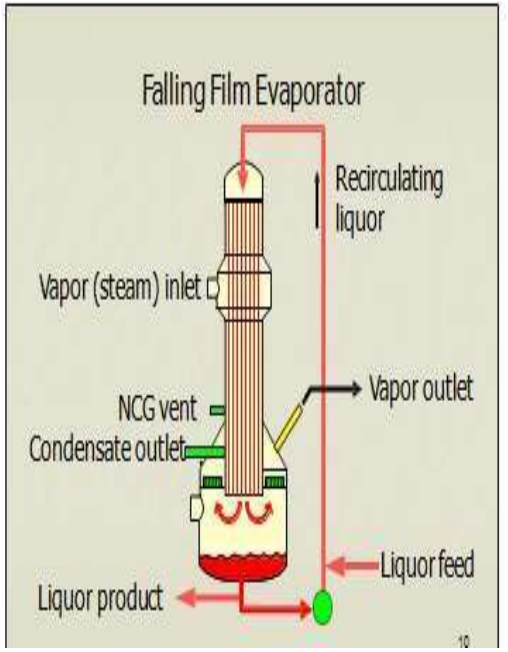


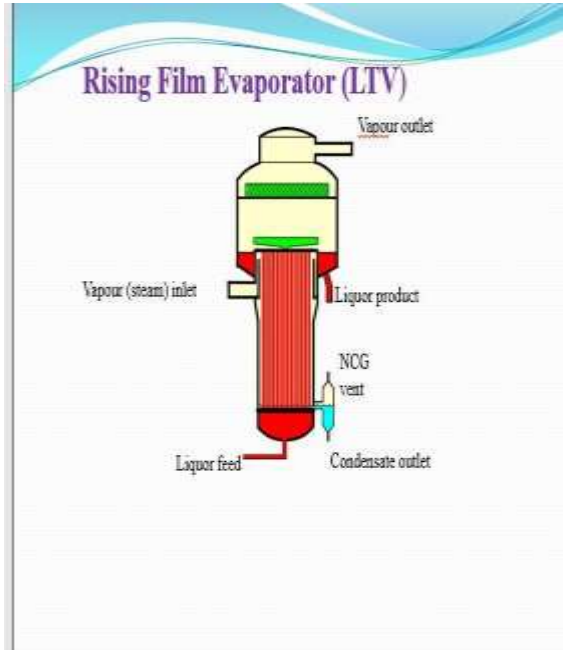
Modern evaporator train



Evaporator types

- Thermal evaporation
  - rising film evaporator
  - falling film evaporator
  - film inside the heating surface
  - film outside the heating surface
- Forced circulation
- Direct contact evaporation
- Mechanical vapor recompression evaporation





Preference of application

Falling Film Evaporator

- Film formed by mechanical (Distribution plate)
- High Turn down can handle higher viscosity (Gravity helps)
- Primary technology worldwide for concentrations up to 50%TS
- Can operate at low ΔT
- Flexible (High turndown)
- Good resistance to scaling
- Moderate HP consumption
- Easily automated
- Foams easily at low %TS

Rising Film Evaporator

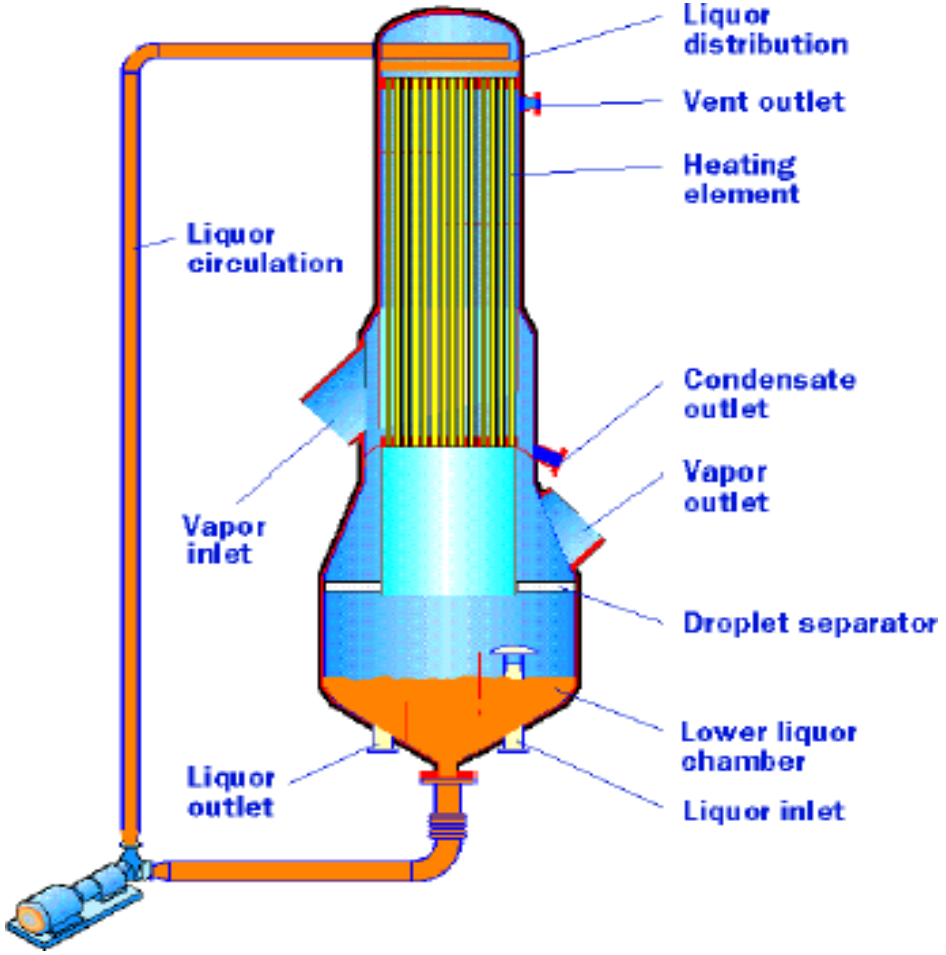
- Liquor film formed by generated vapors from boiling liquor at the bottom of the tubes
- Poor turndown, can't handle high viscosities, minimum ΔT requirement
- Was the workhorse of the Industry, now found only in older mills
- Low operating cost.
- Low propensity for foaming.
- Low liquor viscosity and high flow-rate are ideal conditions.
- Only used today in WBL pre-evaporation where foaming is an issue.

Treatment of foul condensates

- Foul condensates contain
  - methanol
  - malodorous sulfur compounds
  - turpentine
  - red oil (eucalyptus only)
  - water
- Steam is used in the stripper to remove contaminants
- Evaporator and stripper are integrated to get better heat economy
  - located between effects 1 and 2

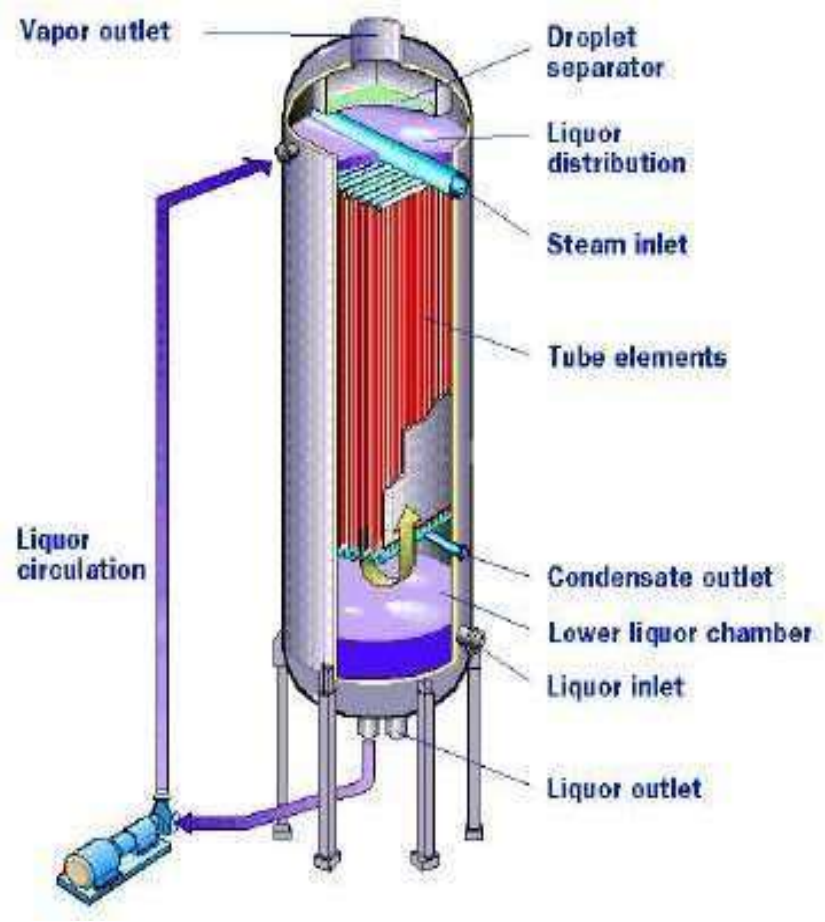
Falling film evaporator - Film inside tubes

- Gravity pulls liquor downwards (window during rain principle)
- Liquor inside the tubes
- Steam outside the tubes
- Fouls with high solids liquor
- Sold as 3 – 7 effects

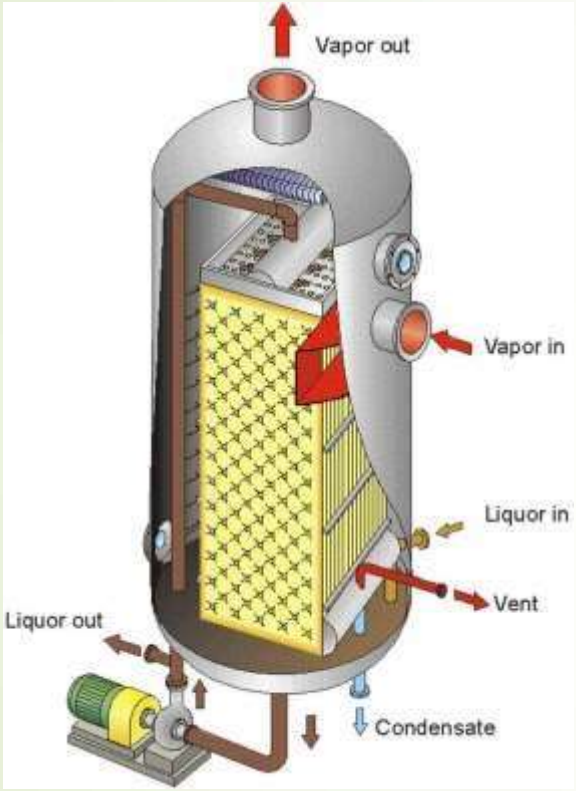


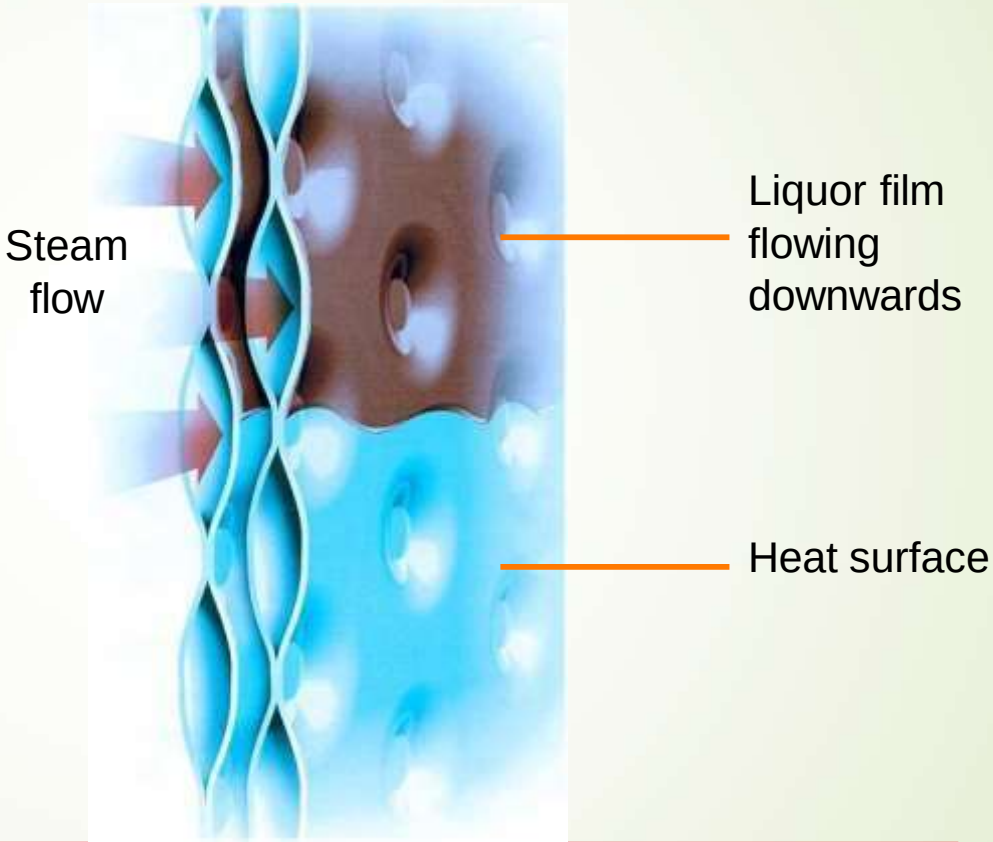
Falling film evaporator - Film outside tubes

- Gravity pulls liquor downwards (window during rain principle)
- Liquor outside the tubes
- Steam inside the tubes
- Used with high solids liquor
- Sold as 1 - 3 effect and as concentrator



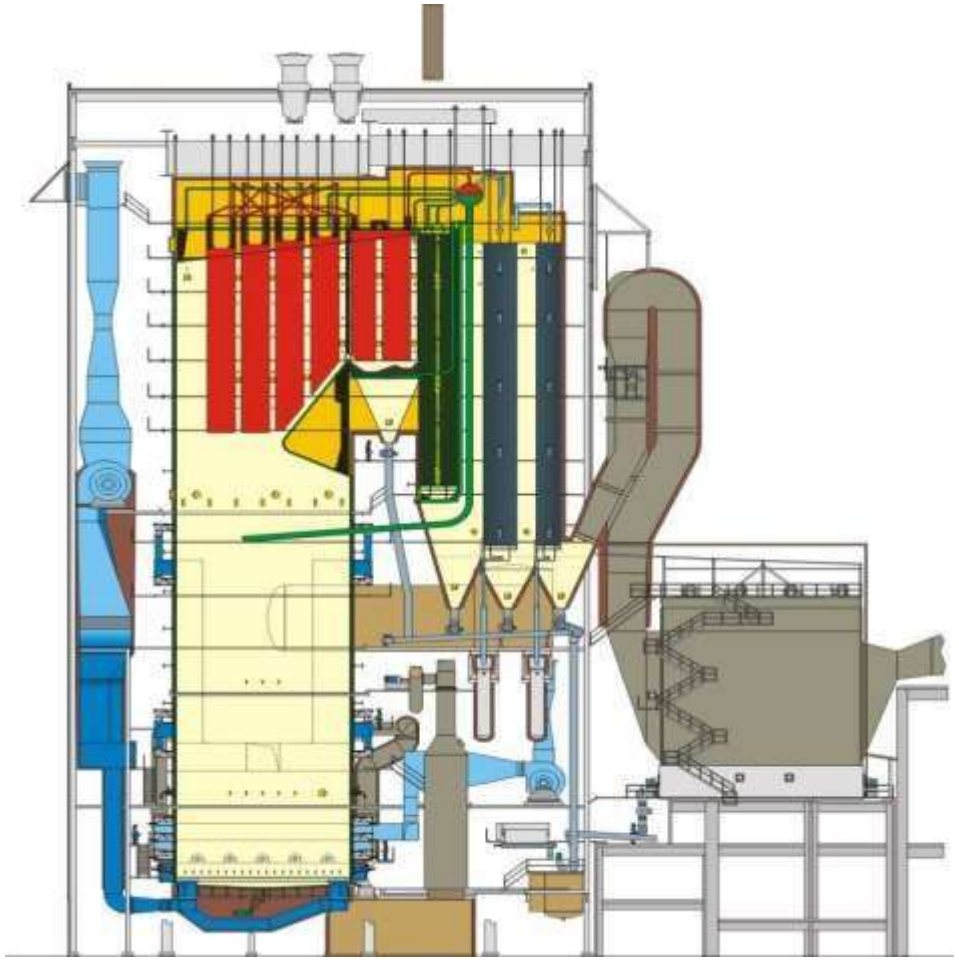
Lamella type evaporator

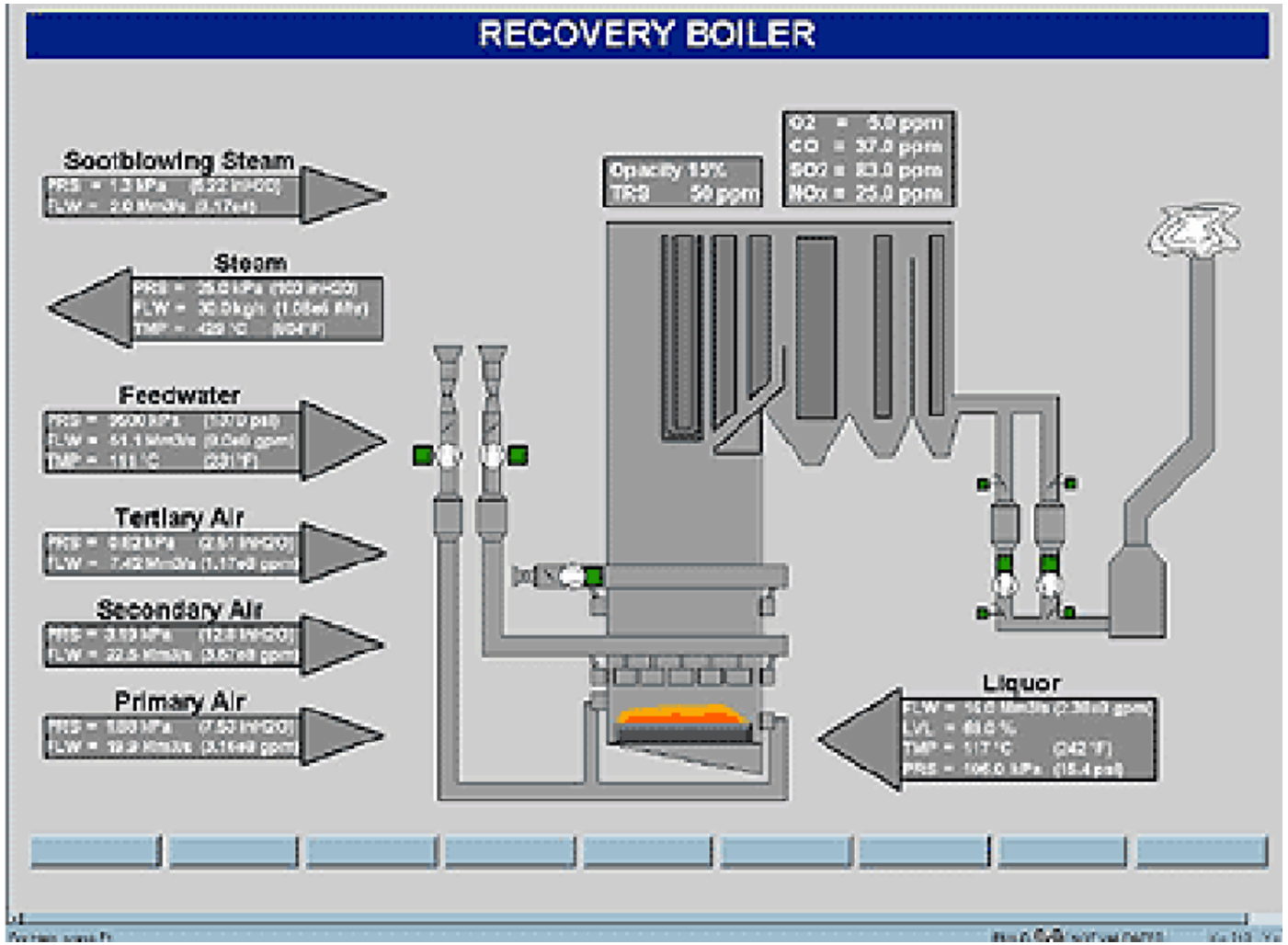




Recovery boiler : Principle of operation

- Recovery Boiler operation of firing Heavy Black Liquor (HBL) to produce steam for power generation and Green liquor

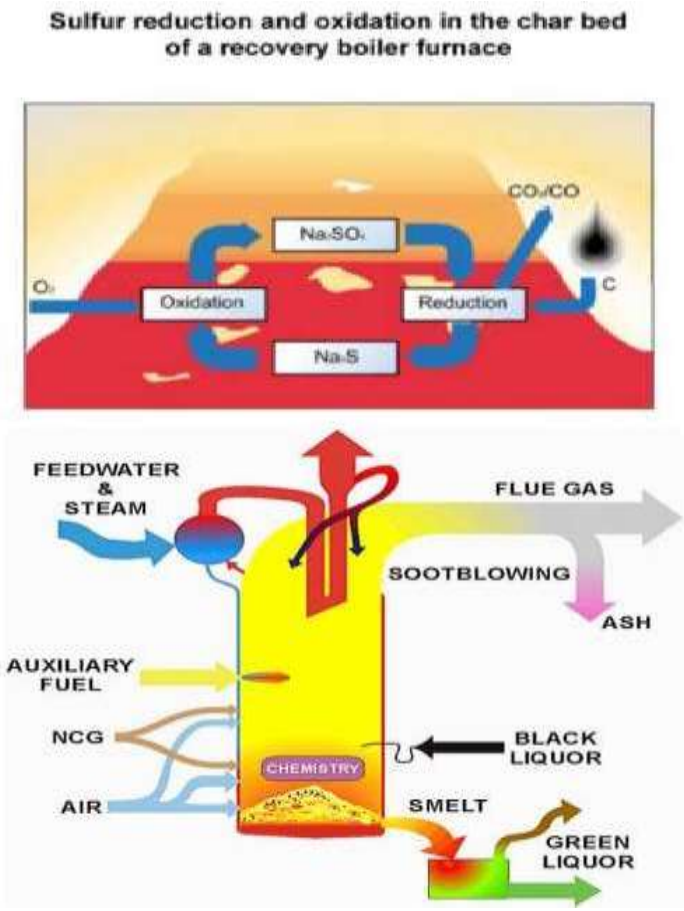




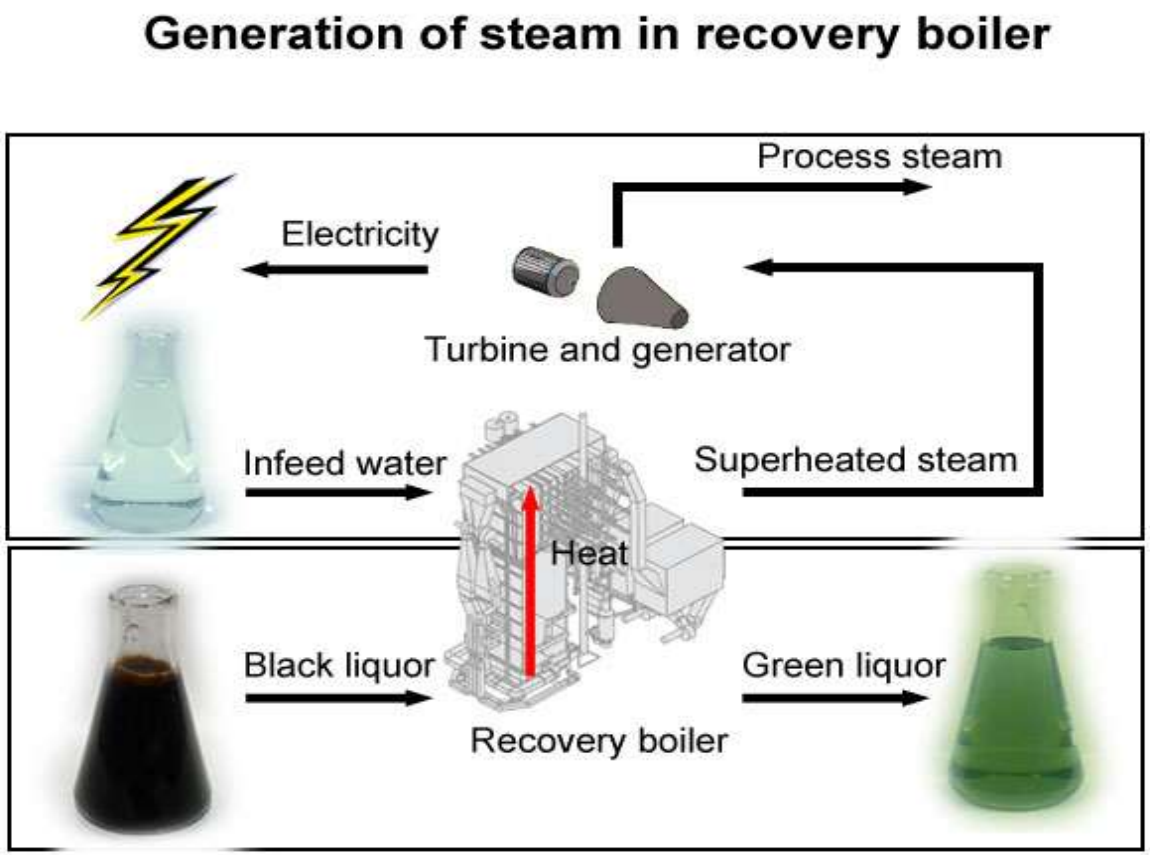
Purpose of the recovery boiler

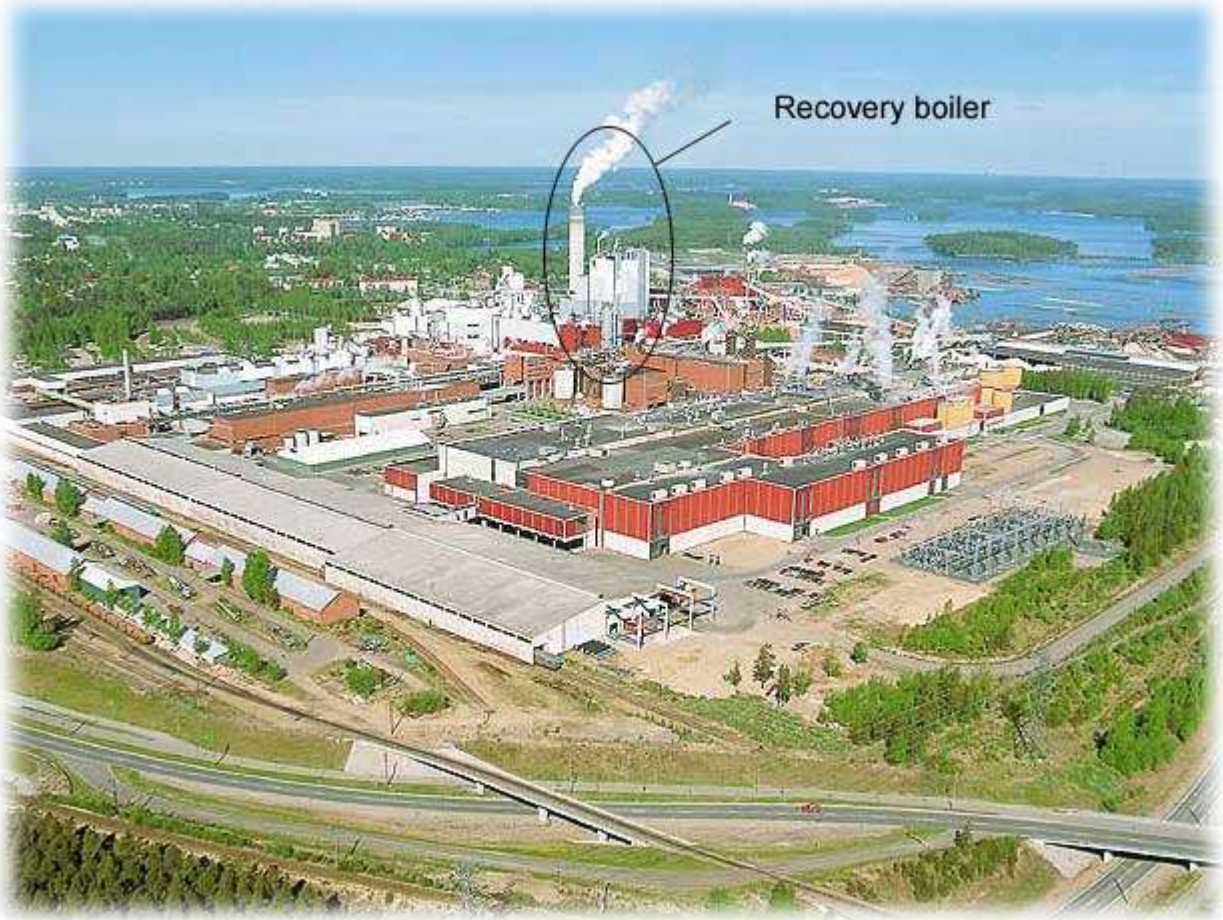
- **Recovery of Chemicals** = **Chemical Reactor**
  - recovery of chemicals from the black liquor through combustion (reduction) to be used for cooking chemical preparation

- **Recovery of Energy** = **Steam Boiler**
  - burn the organic materials in the black liquor and produce energy (steam, electricity)

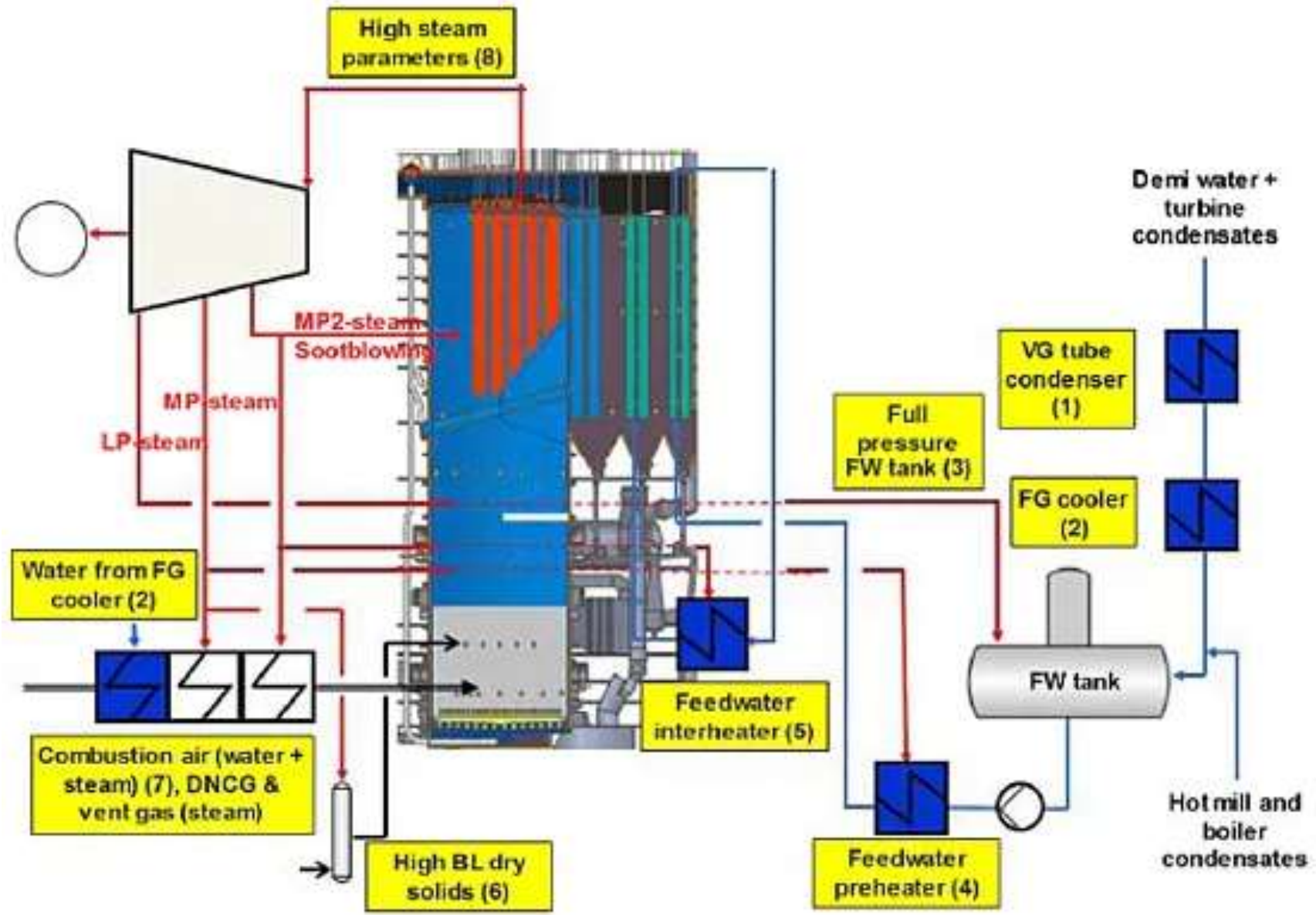


RECOVERY BOILER



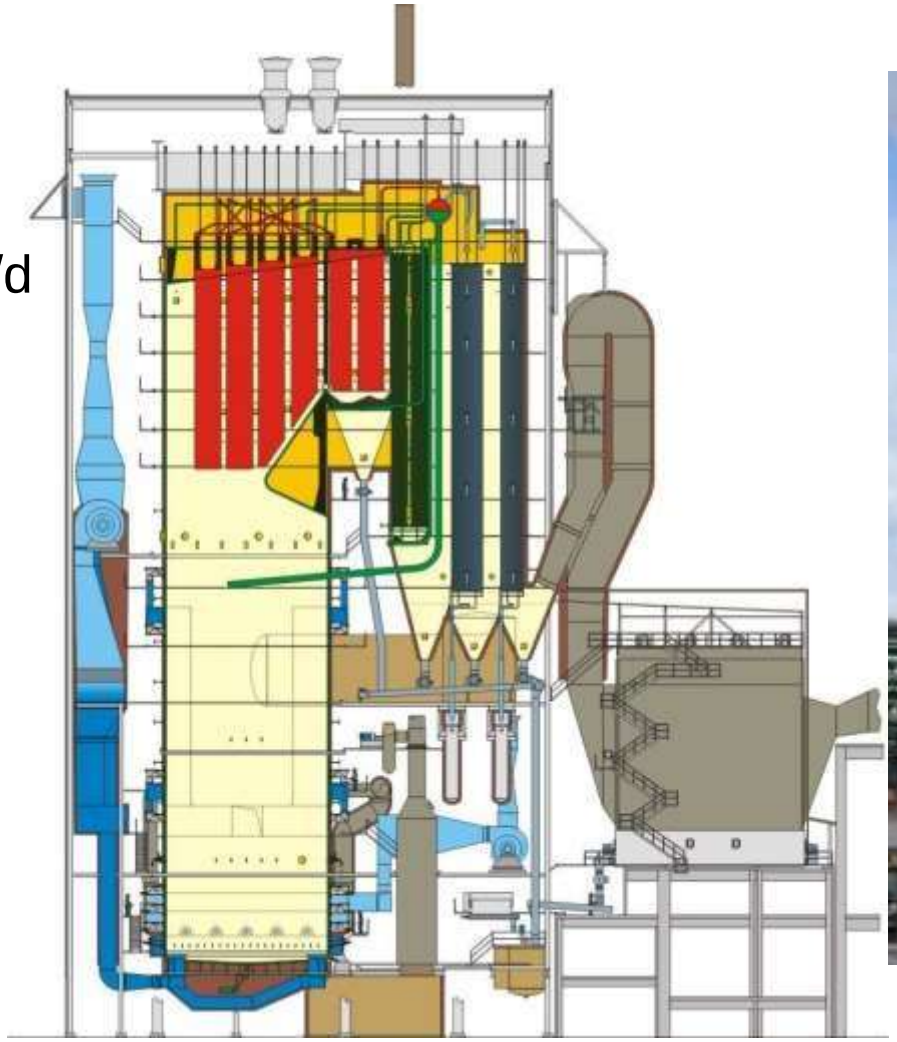


RB / Turbine integration



Modern recovery boiler

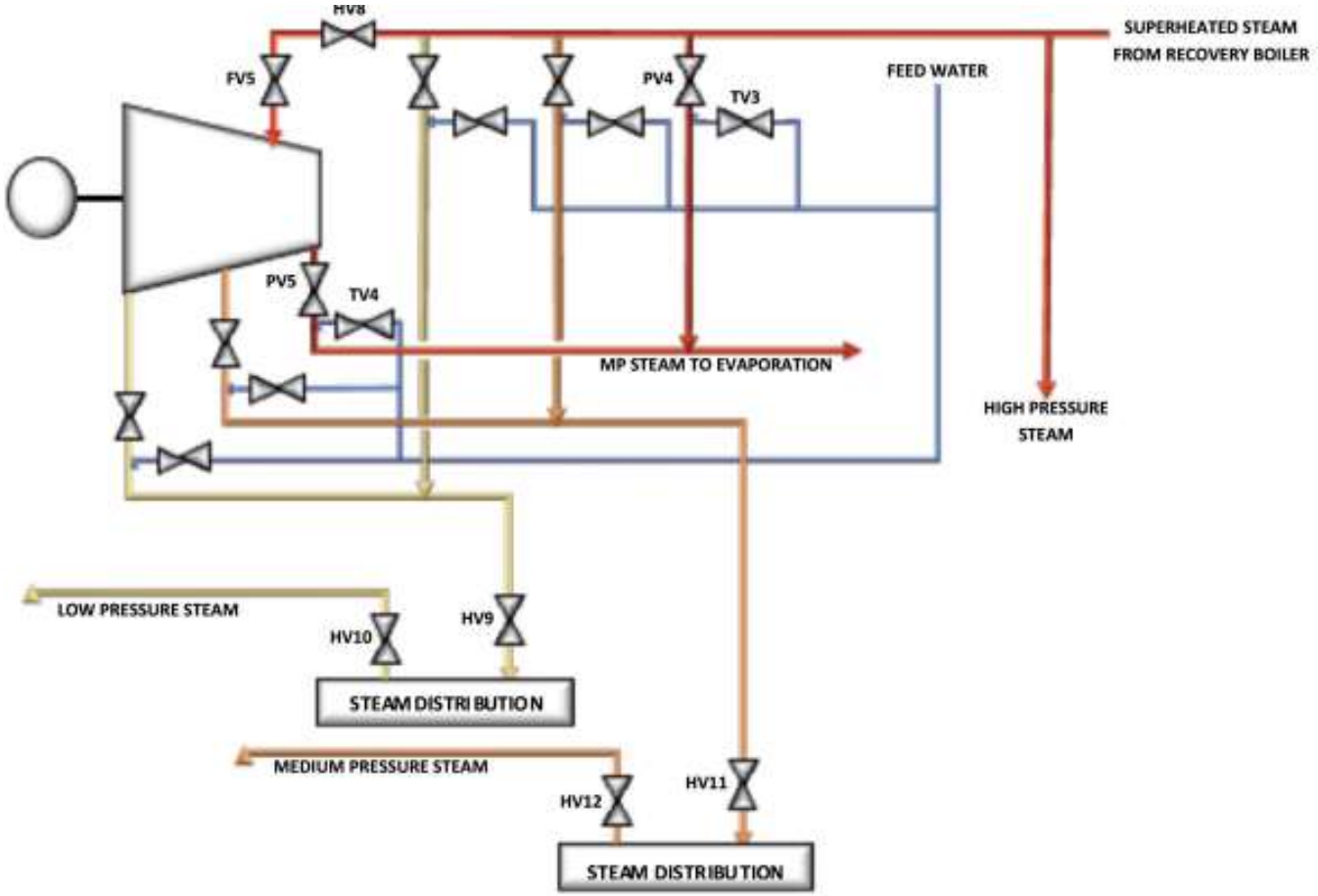
- Steam pressure > 110 bar
- Steam temperature > 515 ˚C
- Capacity > 12 000 tds/d
  - Dry solids content > 80%
- Combustion air from several levels
- DNCG combustion (Diluted gases)
- Additional fuels
  - CNCG (strong gases)
  - methanol
  - turpentine
  - biosludge
  - soap



TURBINE

Steam turbine and generator produce electricity from high pressure and temperature steam (for example 64 Bar / 465 °C). After superheaters the steam has to be well above saturation because moisture causes erosion of blades in steam turbines. Before the turbine a high pressure steam line is directed from the main steam line. Control valve is located before the turbine to control steam flow. The steam temperature and pressure decrease as the steam flows through the blades of the turbine

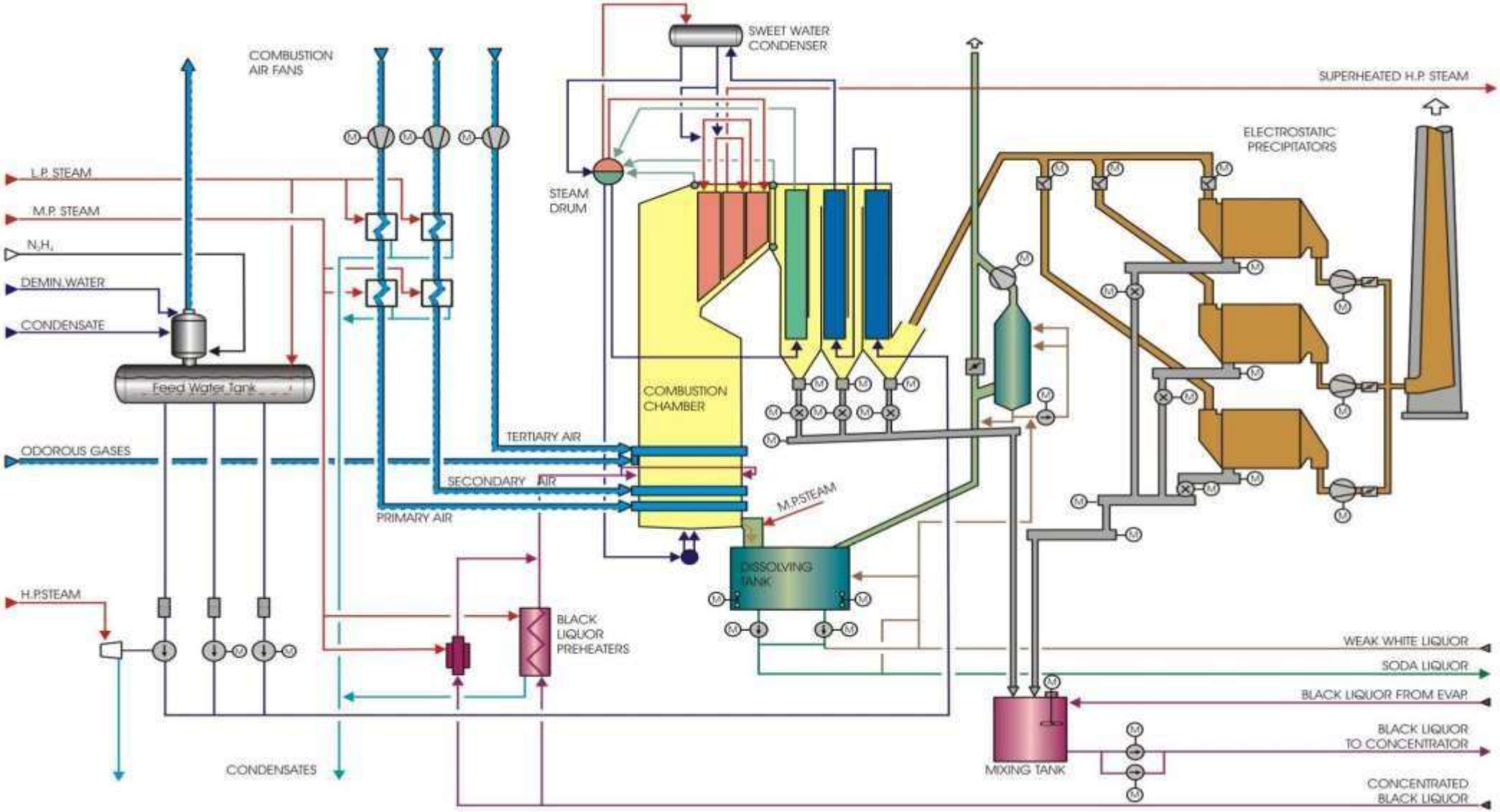
Because the pressure decreases, the volume of the steam increases, increasing its flow rate. The motion energy is utilized in the generator, which transforms the energy of the rotating movement into electric power. Medium pressure steam lines and a low pressure steam line are directed from the main steam line and after the turbine. Feedwater is used for cooling the steam to the correct temperature. The number of steam pipes directed from steam distribution varies and therefore the number of necessary valves after steam distribution varies



Important Equipments:

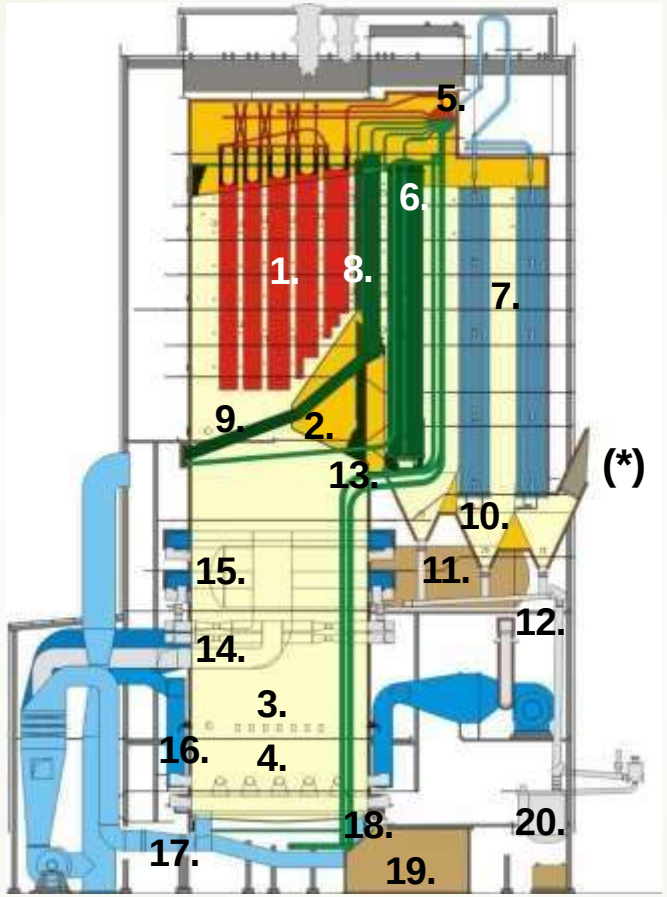
- w a t e r and steam system
- A i r & f l u e g a s System
- B l a c k liquor system
- S p o u t s and dissolving tanks
- S o o t blowers
- E l e c t r o static precipitator
- H e a t exchanger

Recovery boiler process



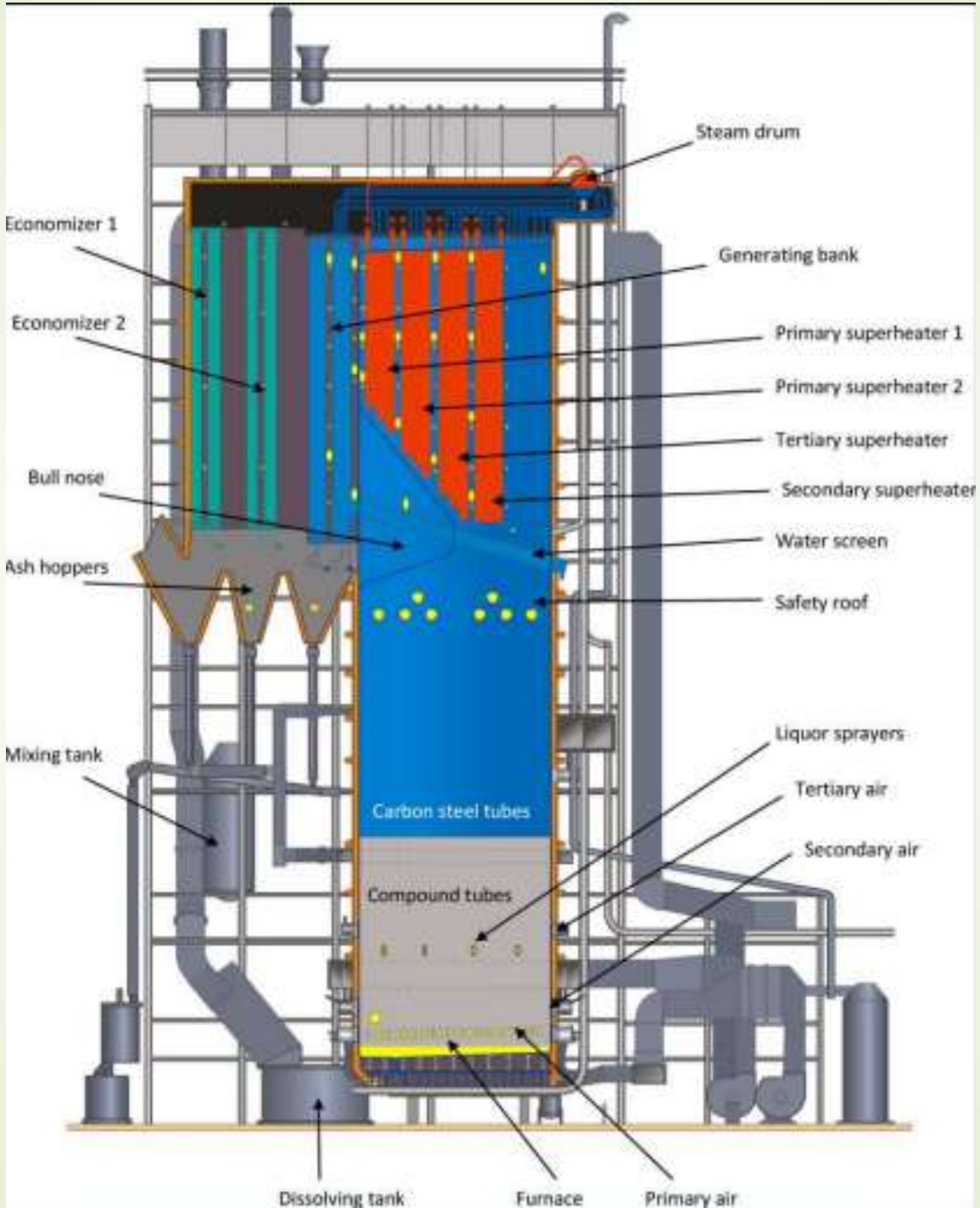
Recovery boiler main parts

1. Superheaters (1B, 2, 3, 4, 1A)
2. Bullnose/nose arch
3. Black liquor nozzle openings
4. Start-up burners



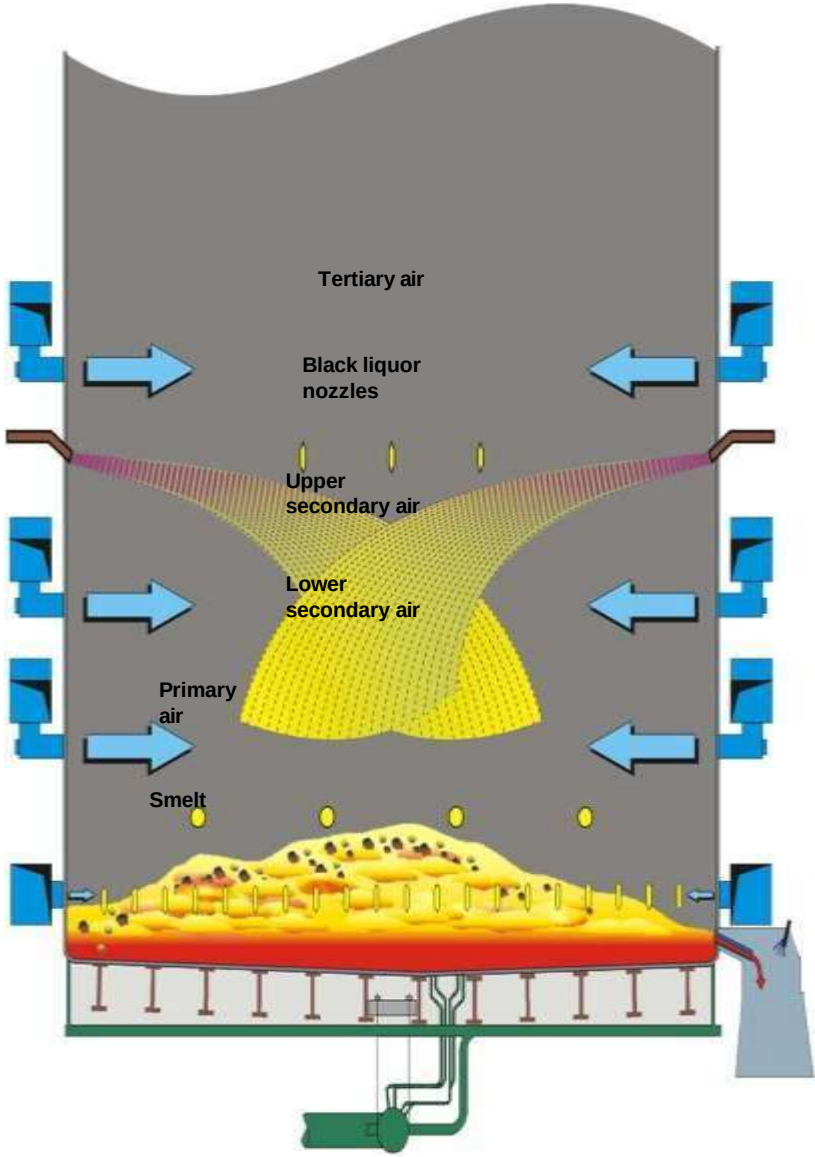
5. Steam drum
6. Boiler generating bank
7. Economizers 1 and 2
8. Rearwall screen
9. Furnace screen
10. Ash hoppers (3 pcs.)
11. Feedwater tank
12. Ash conveyors
13. Downcomers
14. NCG ducts
15. Tertiary air ducts
16. Secondary air ducts
17. Primary air ducts
18. Smelt spouts
19. Dissolving tank
20. Mixing tank

(*) Electrostatic precipitator


Steam drum
Economizer 1
Generating bank
Economizer 2
Primary superheater 1
Primary superheater 2
Tertiary superheater
Bull nose
Secondary superheater
Water screen
Ash hoppers
Safety roof
Liquor sprayers
Mixing tank
Tertiary air
Carbon steel tubes
Secondary air
Compound tubes
Dissolving tank
Furnace
Primary air

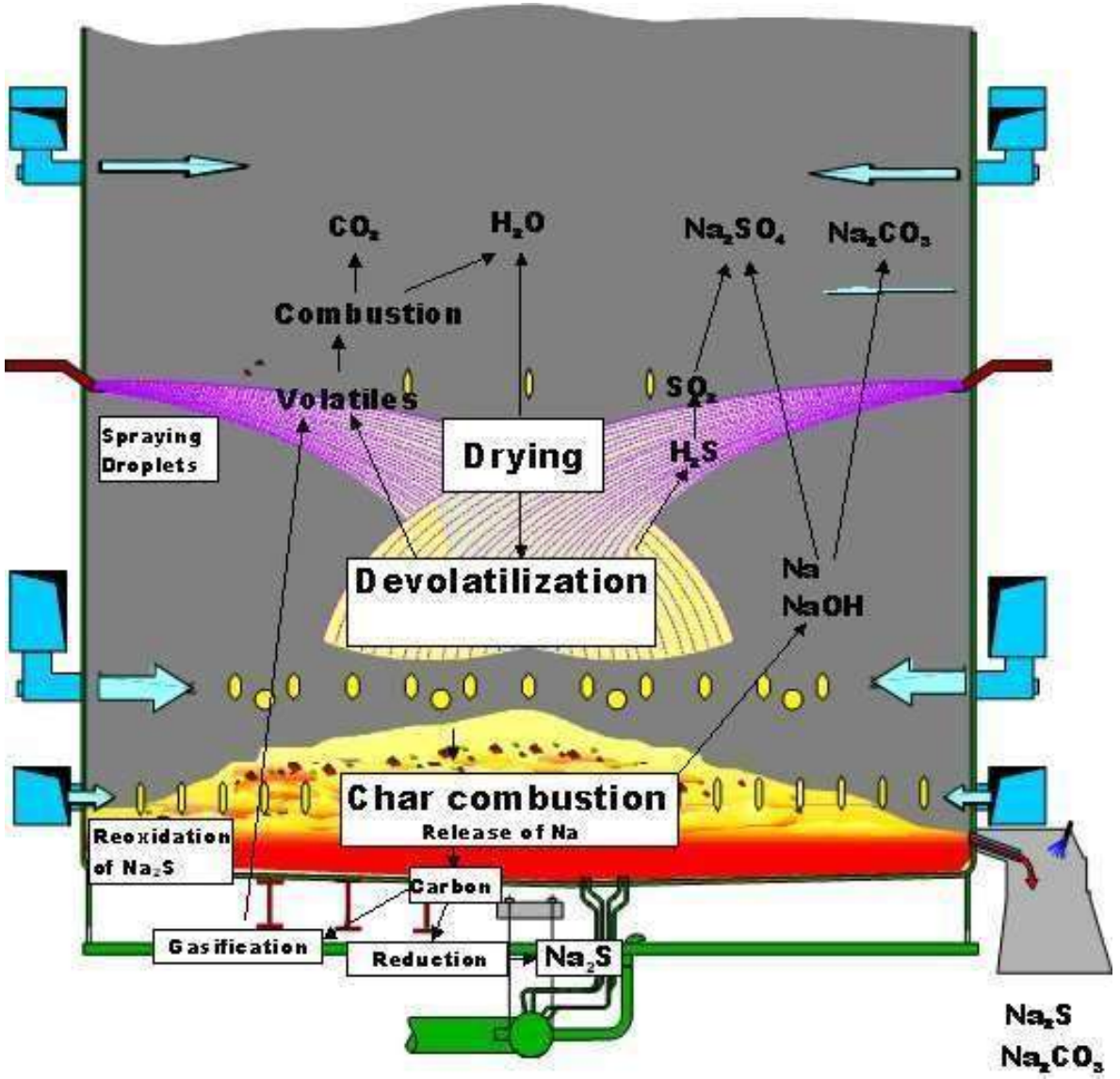
Furnace process

- Black liquor is injected into the recovery boiler from a height of 5…8 meters
- Combustion air is injected at three different zones in the boiler
- Burning black liquor forms the char bed at the bottom of the boiler, where complicated reactions occur
- Smelt is drained from the boiler and is dissolved with weak white liquor to form green liquor, which contains the recovered cooking chemicals
- High pressure steam is generated from feed water by heat releasing from combustion reactions



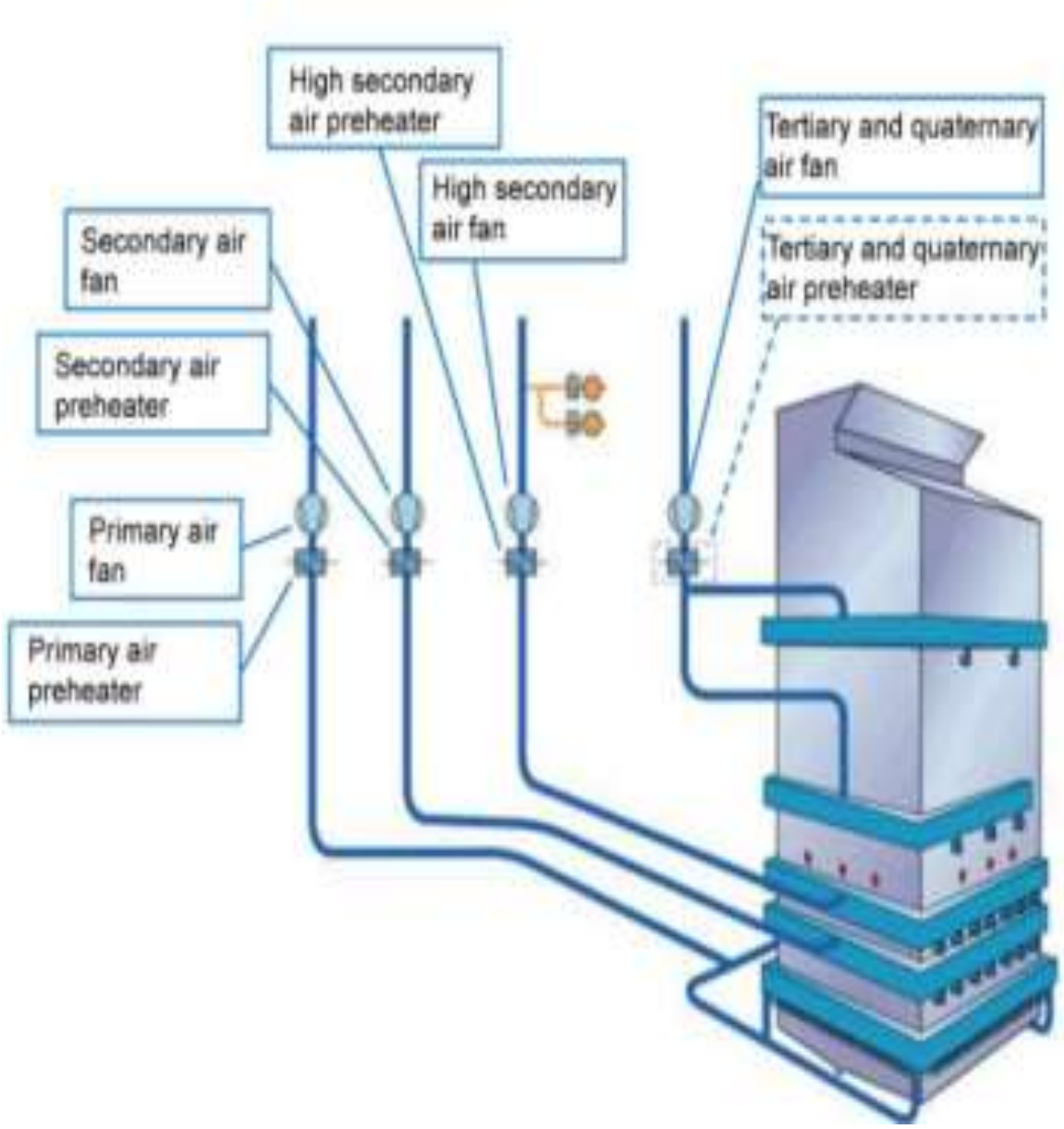
Chemical reactions in furnace

- Drying
  - water is evaporated
- Devolatilization
  - droplet size increases
  - gases are released
- Char burning
  - carbon is burned off
  - inorganic salts melt, reactions
- Upper furnace reactions
  - volatiles combustion
  - formation of sodium sulphate and sodium carbonate

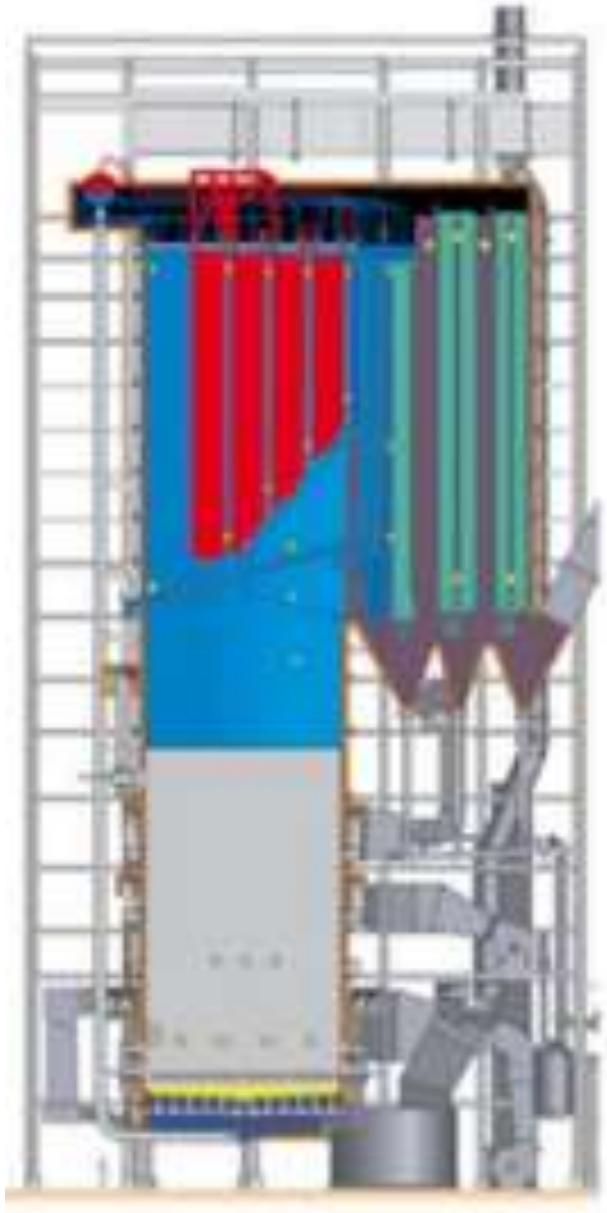


Role of Air system:

Primary air	• **Primary air controls the char bed of perimeter.** • **Primary air keeps smelt hot and fluid.** • **Hot air improves combustion stability.**
Secondary air	• Control the char bed height • Secondary air burns char and volatiles
Tertiary air	• Complete mixing and burning of Combustible Gases (CO ,H2S) • It is essential for staged combustion



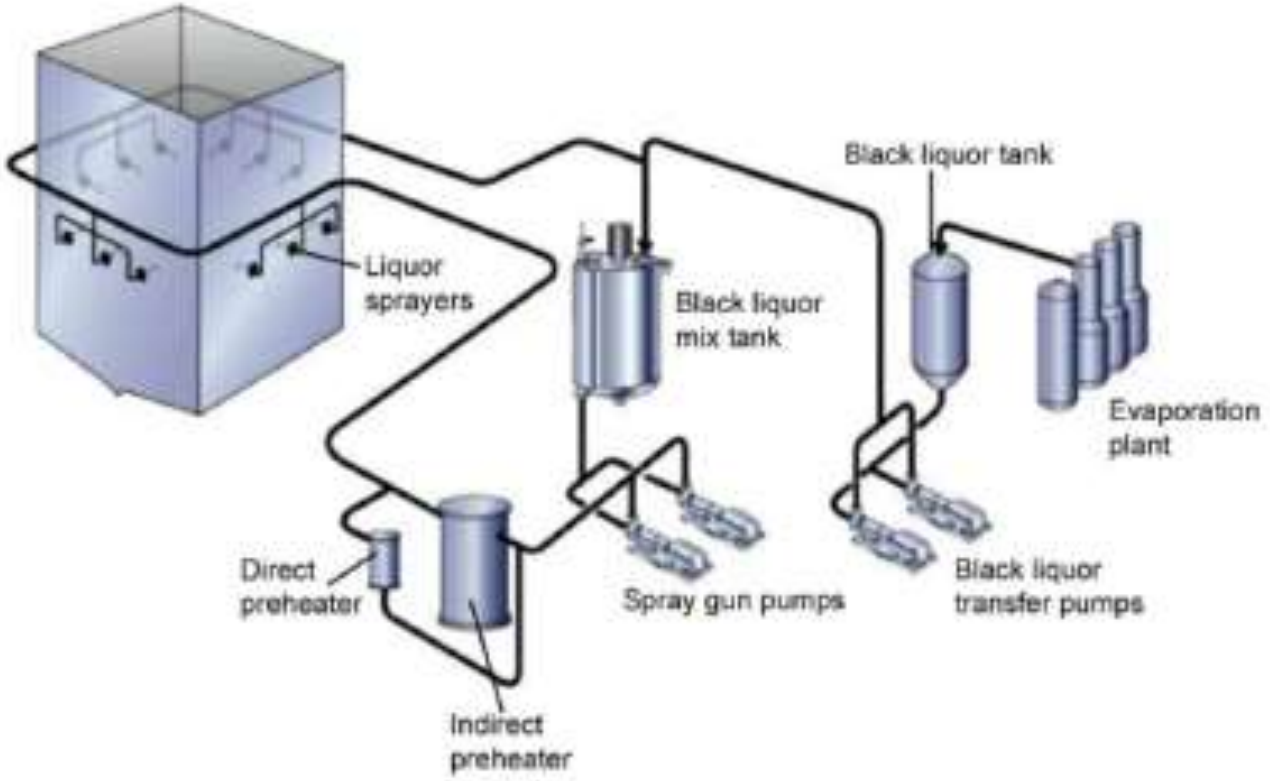
RB – MULTI FUEL BOILER

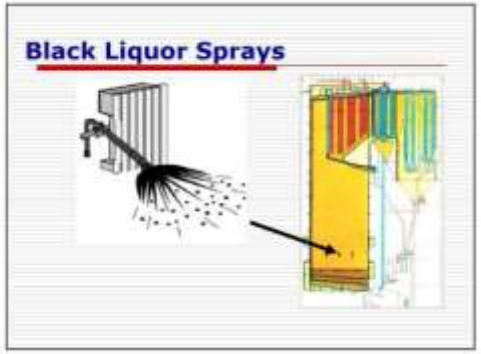


- Black liquor
- Oil
- Natural gas
- CNCG
- DNCG
- Vents (dissolving and mixing tank)
- Biosludge
- Soap
- Turpentine
- Methanol

Black liquor system:

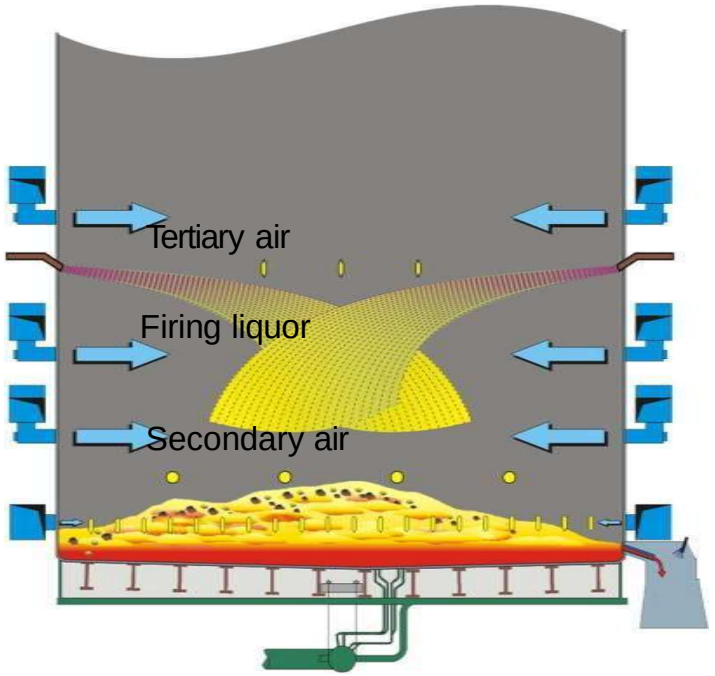
- Black liquor system preparing liquor for firing.
- It contains Firing pump, AMT, Indirect heater ,Direct heater and Spray guns.
- HBL concentration 65% to 85% and liquor temperature is 125 to 148 deg Celsius.

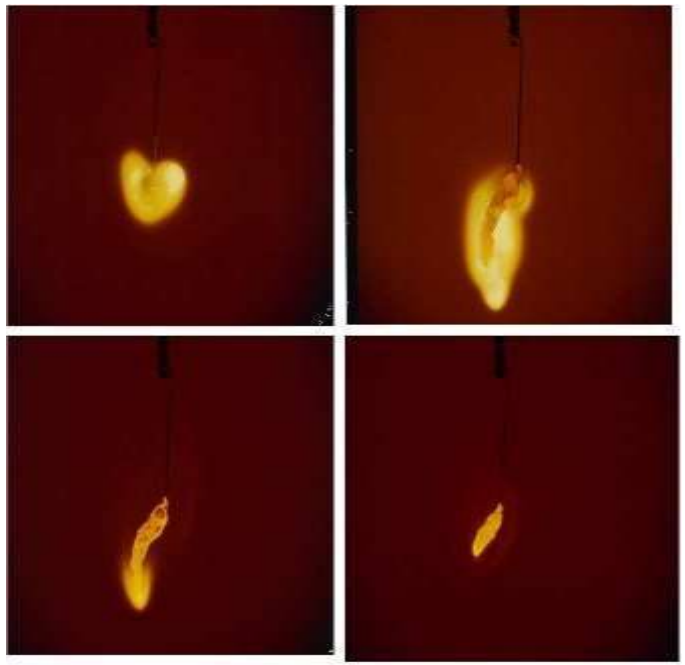




Liquor spraying

- Target
  - spray the liquor evenly on the char bed
  - optimize the droplet size
- Liquor gun openings on all walls
- Locations adjusted to the air system between secondary and tertiary air ports

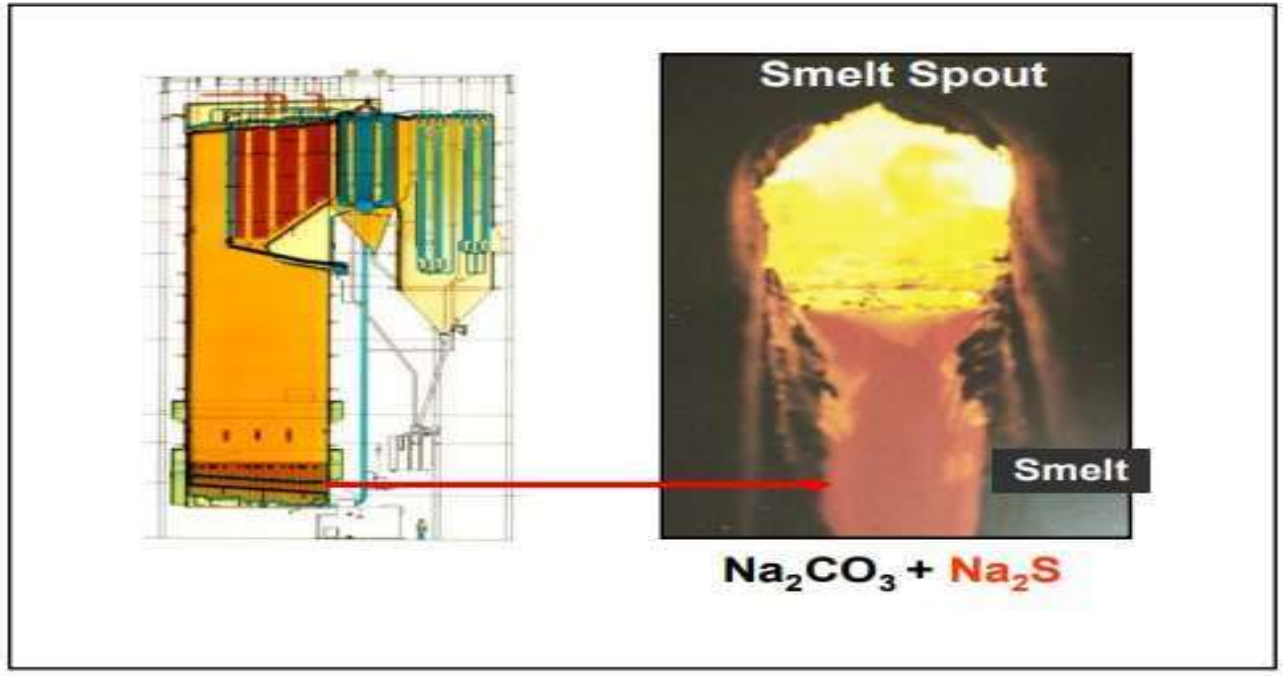


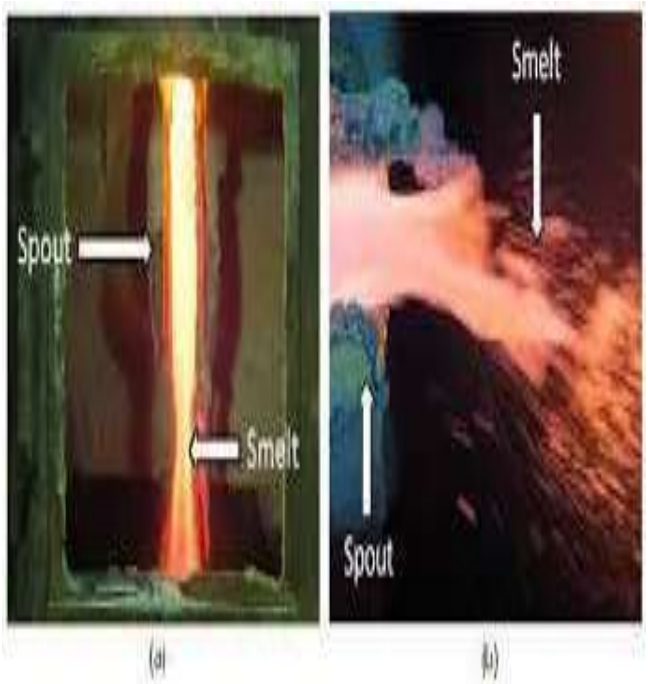


Spout system:

Molten smelt is produced within the recovery boiler is removed from the furnace through the smelt spouts into a dissolving tank, where its is dissolved to form green liquor.

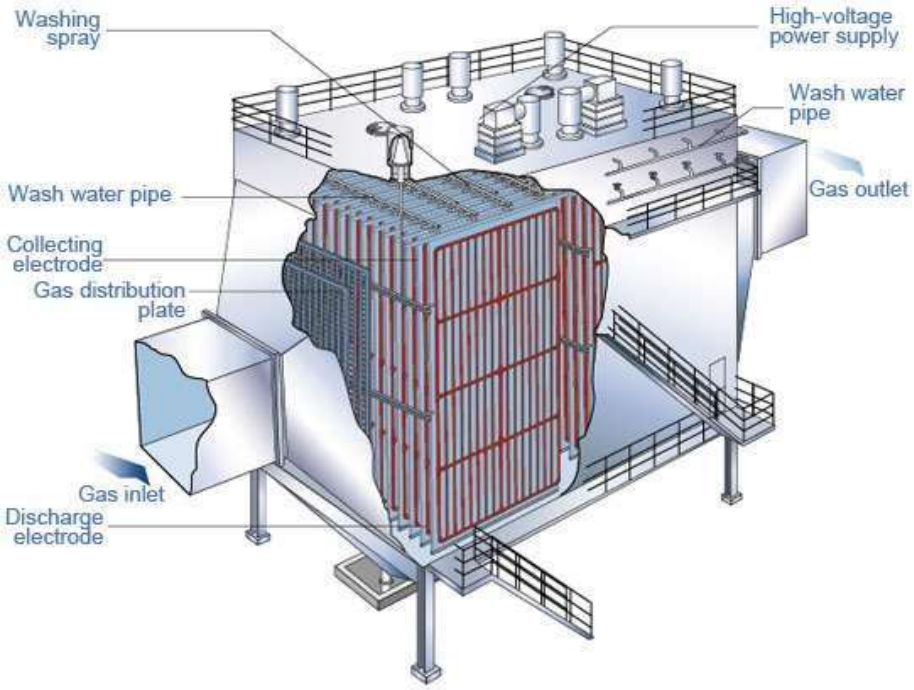
- Smelt shattering jets are used to break the smelt stream as it comes out of he furnace, to prevent the accumulation of the molten smelt within the dissolving tank

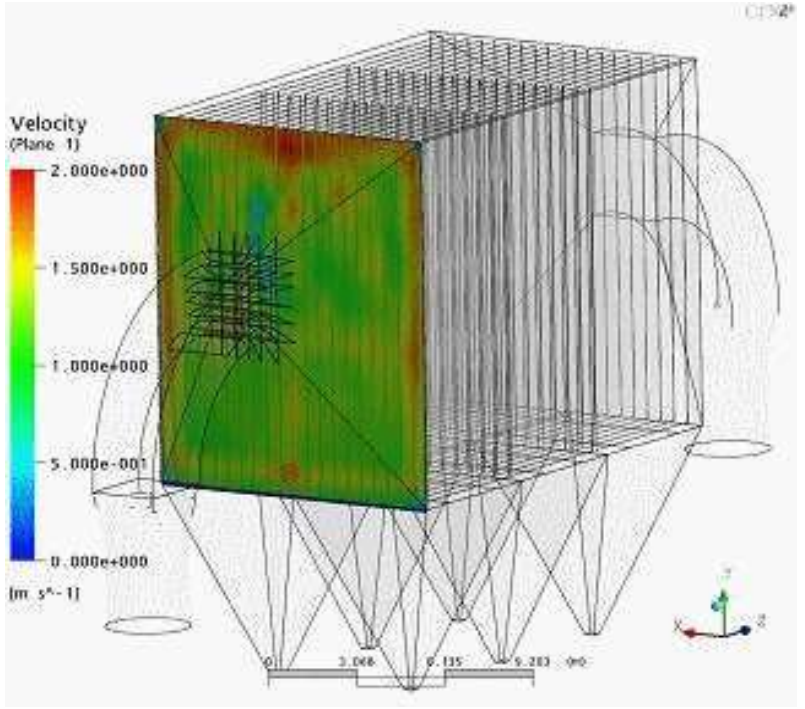




Electrostatic precipitator :

An **electrostatic precipitator** (**ESP**) is an device that removes dust particles from a flowing gas (such as air) using the force of an **induced electrostatic** attraction



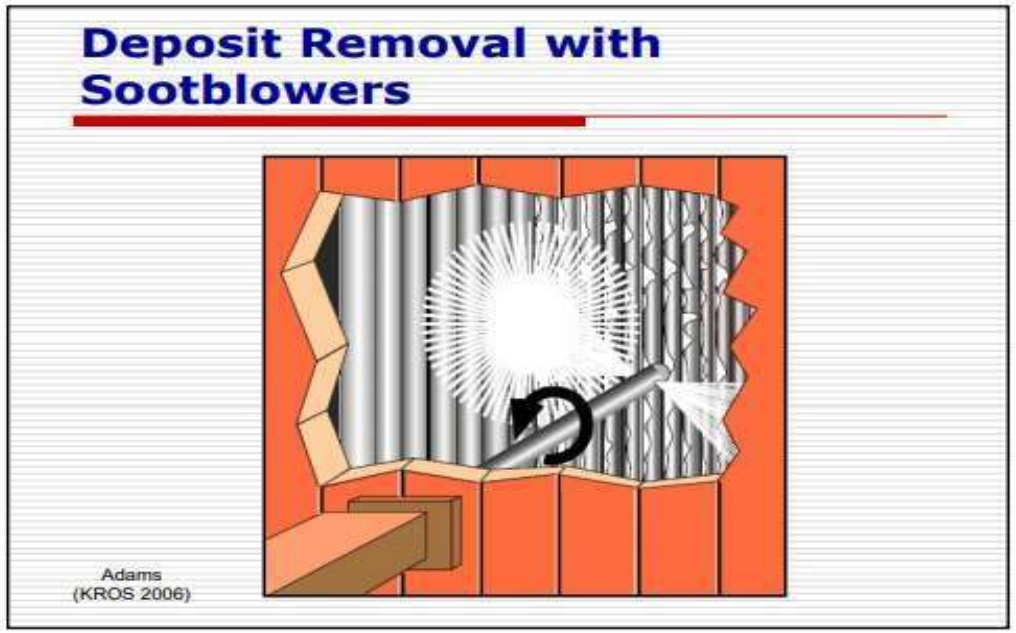


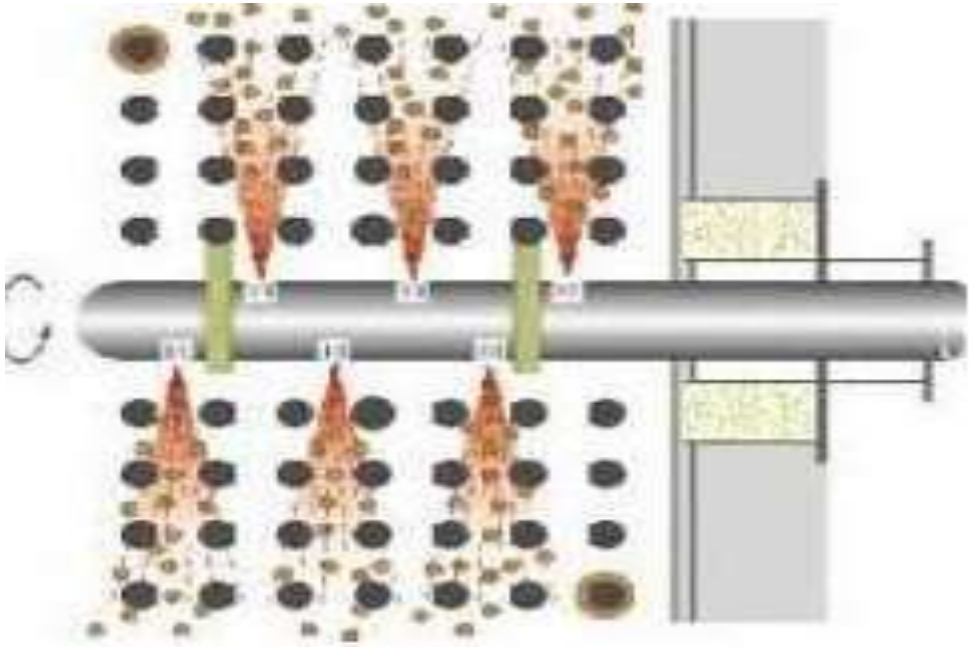
Smelt-water explosion

- Even a small amount of water mixed with molten smelt at high temperature can cause it
  - purely physical phenomenon
- Water turns into steam in few ms
  - sudden evaporation causes increase of volume and a pressure wave of 10 - 100 000 Pa
  - sufficient to cause furnace walls to bend
- Furnace equipped with a weak corner to control the direction of explosion

Soot blower:

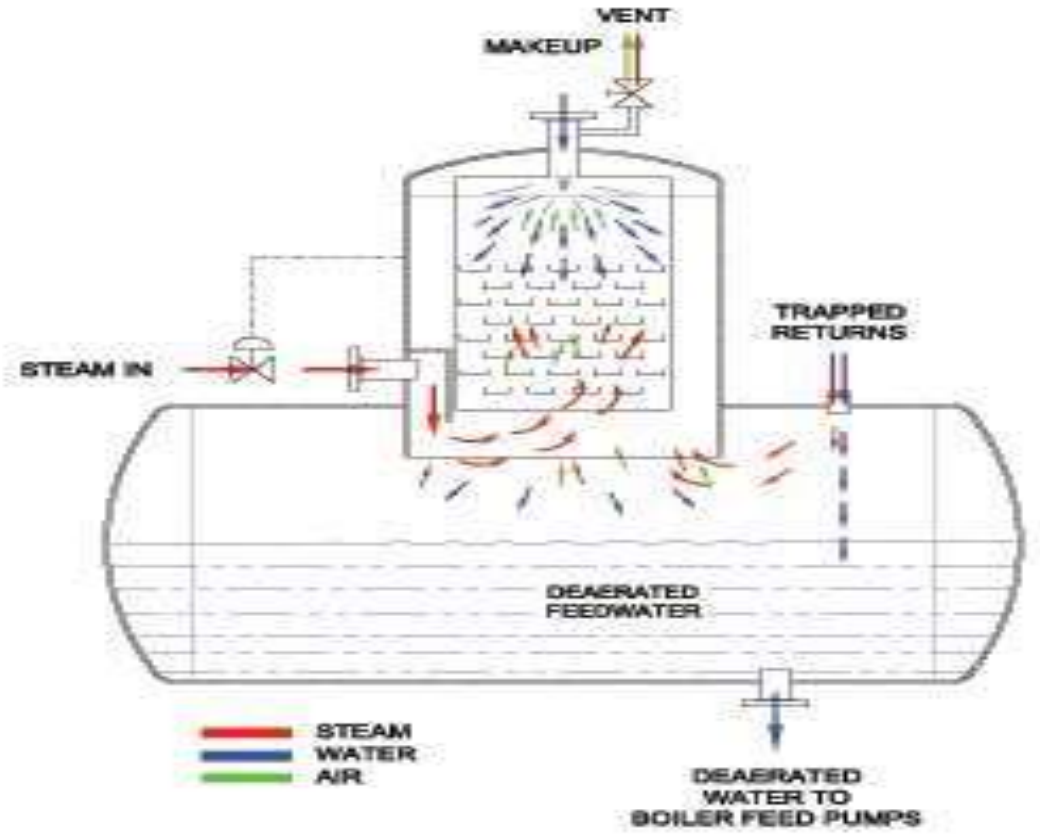
- A **soot blower** is a device for removing the **soot** that is deposited on the furnace tubes of a boiler during combustion.
- Wall Blowers also known as IRs (Insertable Rotating)
- Long Retractable Soot Blower (LRSB)
- Air Heater Blower.
- Steam blowing medium (steam)





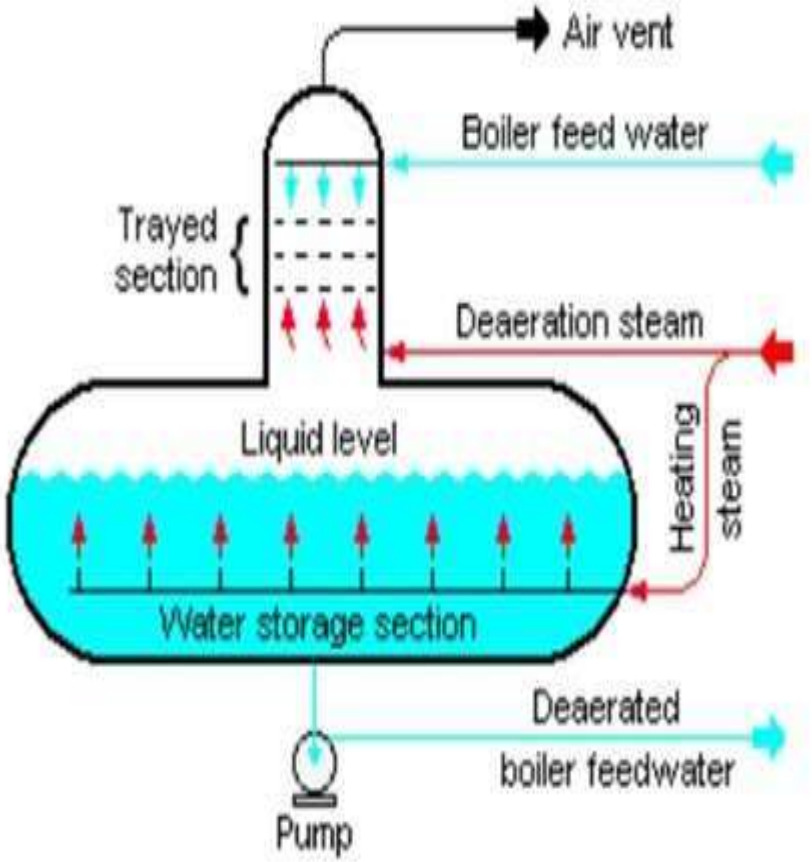
Deaerator:

- A deaerator is a device that removes oxygen and other dissolved gases from water, such as feed water for steam-generating boilers.
- Dissolved oxygen in feedwater will cause serious corrosion damage in a boiler by attaching to the walls of metal piping and other equipment and forming oxides (rust).
- Dissolved carbon dioxide combines with water to form carbonic acid that causes further corrosion



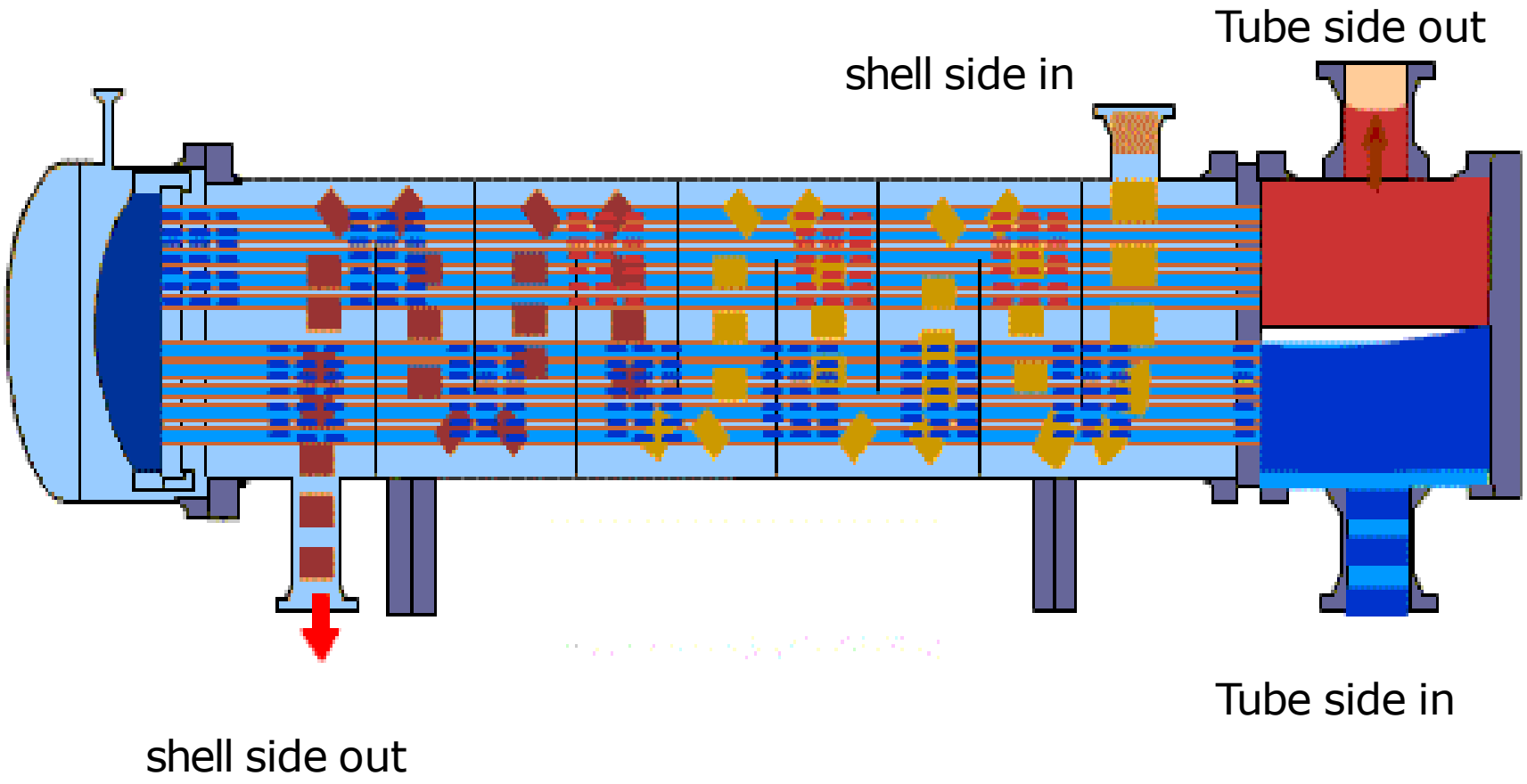
Deaerator:

- Oxygen scavenging chemicals are very often added to the de aerated boiler feed water to remove any last traces of oxygen that were not removed by the de aerator.
  - sodium sulfite (Na_2SO_3),
  - hydrazine (N_2H_4), Ethylenediaminetetraaceticacid (EDTA),
  - Diethyl hydroxylamine(DEHA),
  - Nitrilotriacetic acid (NTA)



Indirect heat exchanger:

- A heat exchanger is a device used to transfer heat between two or more fluids.
- Types of flow are Counter Flow ,Co current Flow and Cross flow



Boiler accessories:

Air pre heater:

- The function of air pre-heater is to increase the temperature of air before entering the furnace.

Economizer:

- waste heat of the flue gases is utilised for heating the feed water.
- To recover some of the heat being carried over by exhaust gases.
- heat is used to raise the temperature of feed water supplied to the boiler.
- Evaporative capacity of the boiler is increased.
- Overall efficiency of the plant is increased.

Boiler accessories:

Super heaters:

- super heater is to increase the temperature of the steam above its saturation point.
- Super heaters are heat exchangers in which heat is transferred to the saturated steam to increase its temperature.

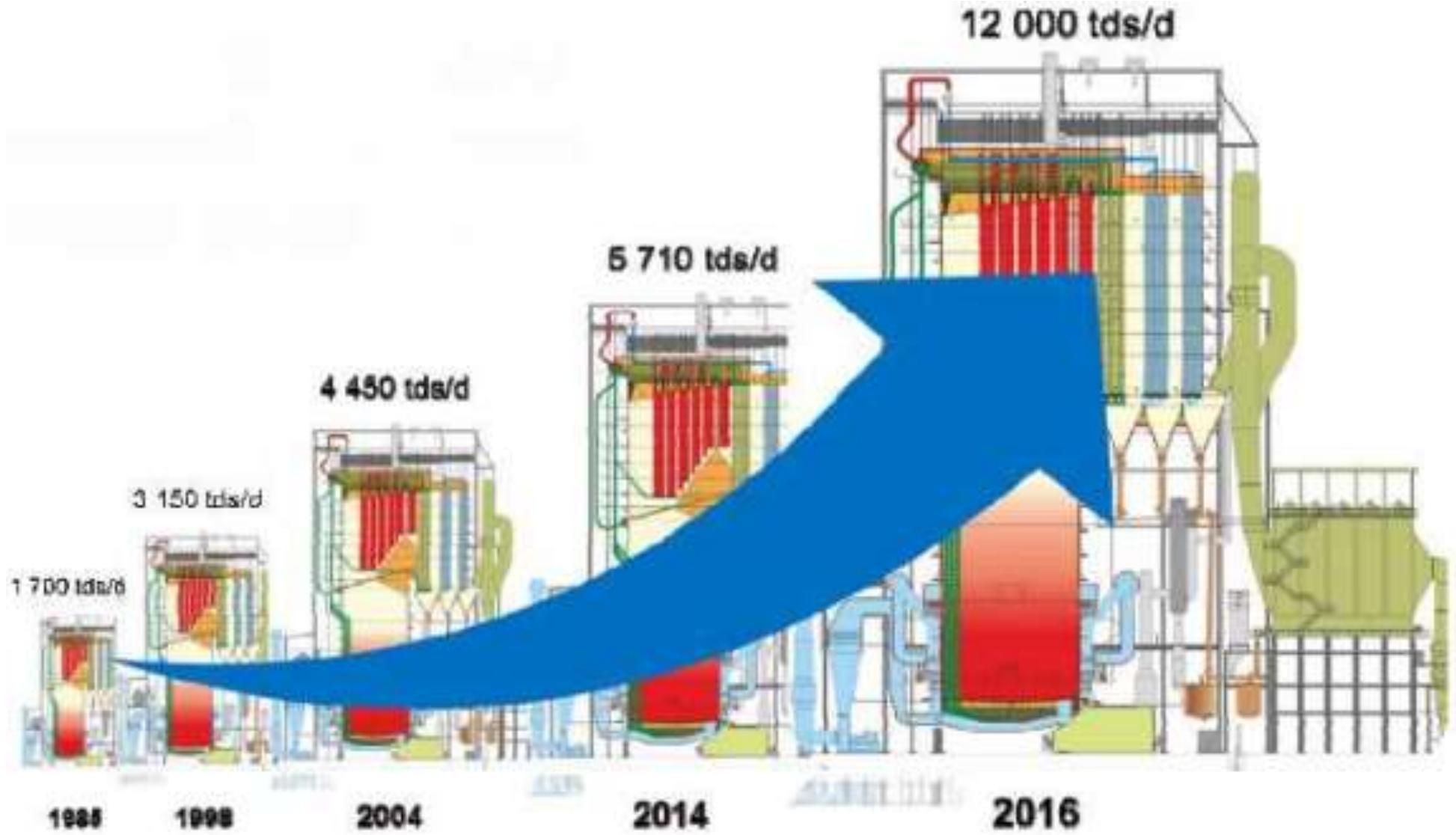
Feed water pump:

- Feed pump is a pump which is used to deliver feed water to the boiler.

Useful numbers

• ADt (bleached)	1.3 - 2.0	Tds / T
• Dry solids (virgin)	65 - 83	%
• Density	1.35 - 1.43	kg/l
• HHV	13.0 - 15.0	MJ/kgds
• Furnace bottom loading	18 - 25	$tds/d/m^2$
	3.0 - 4.0	MW/m^2
• Steam production	3.0 - 4.5	kg/kgds

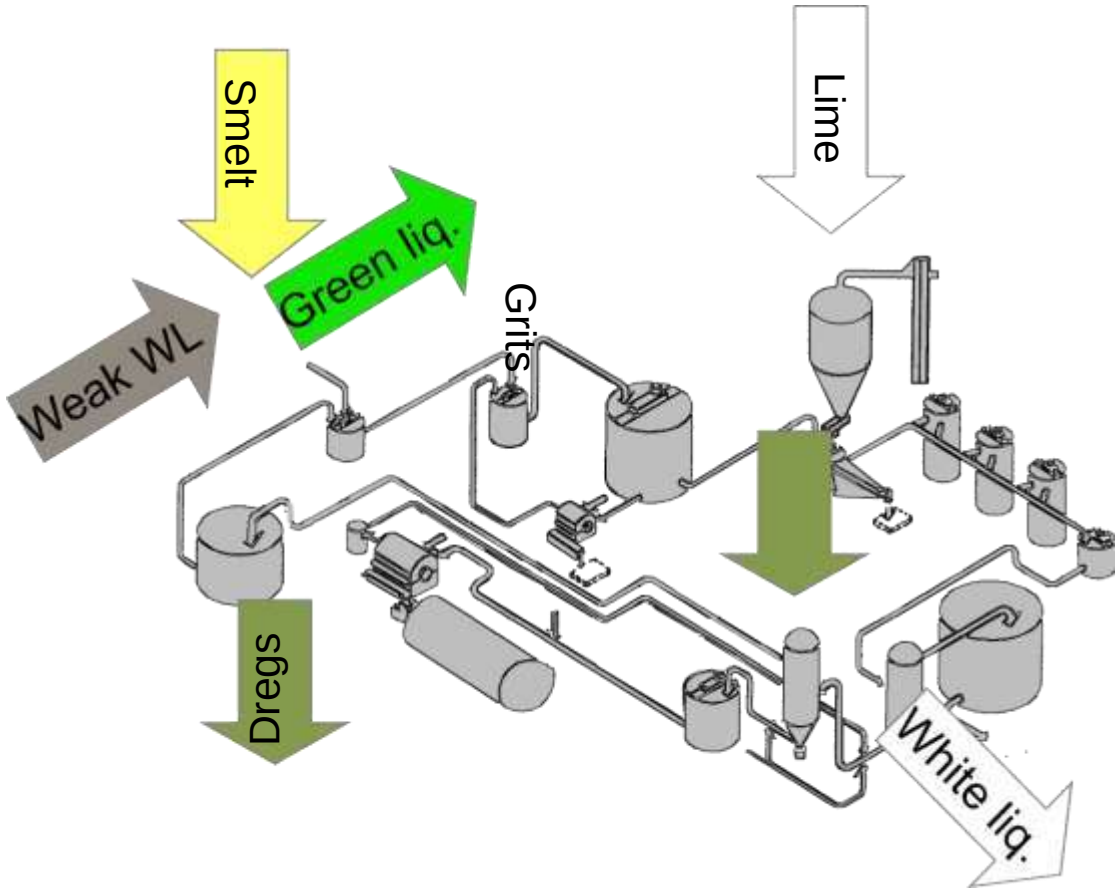
RB CAPACITY DEVELOPMENT



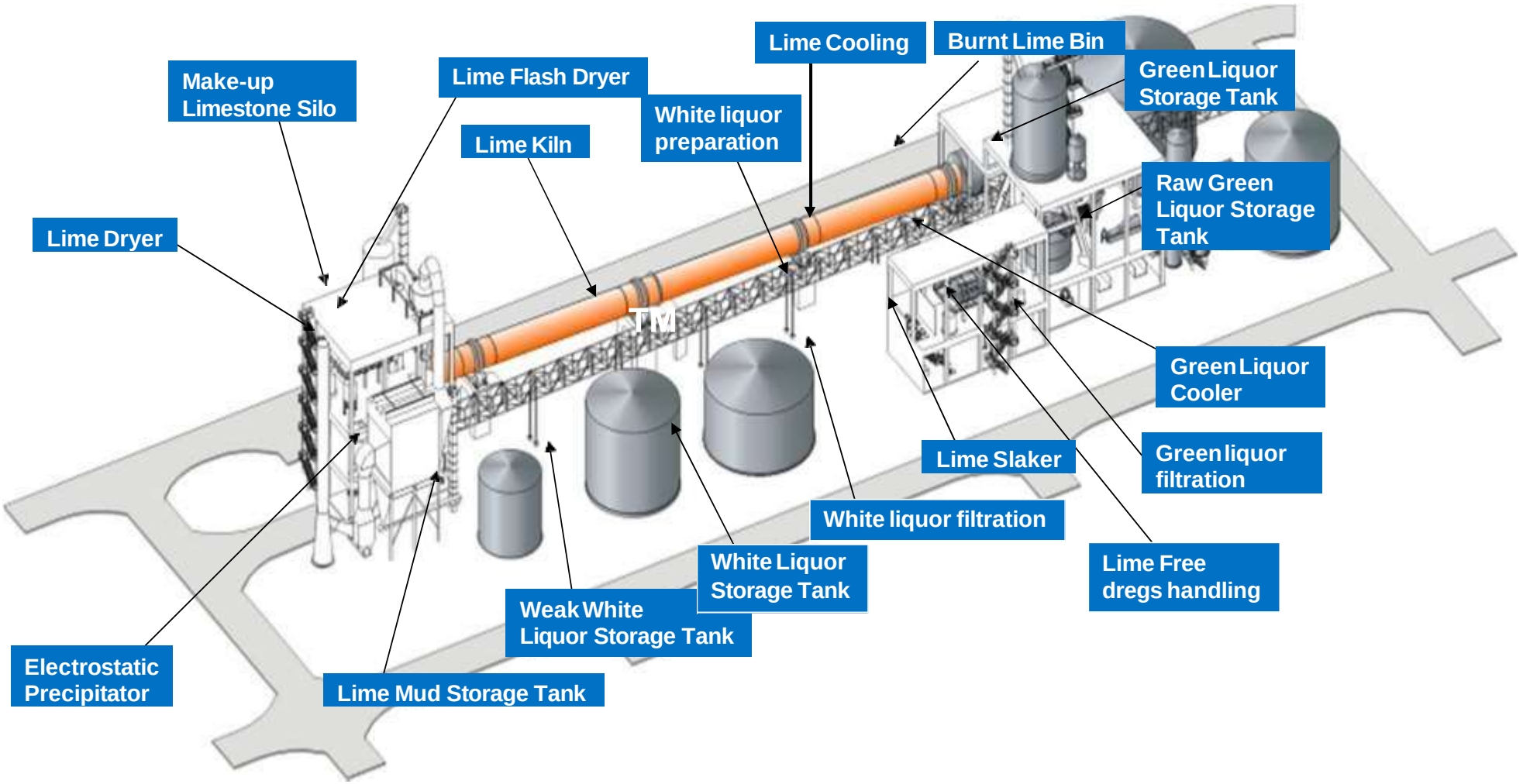
Re causticizing Plant

Mission:

- Production of white liquor for cooking by converting sodium carbonate to hydroxide with lime and removal of non process elements



Modern white liquor plant



Key terms to know:

TTA = TOTAL TITRATABLE ALKALI

$NaOH + Na_2S + Na_2CO_3$

AA = ACTIVE ALKALI

$NaOH + Na_2S$

EA = EFFECTIVE ALKALI

$NaOH + ½\ Na_2S$

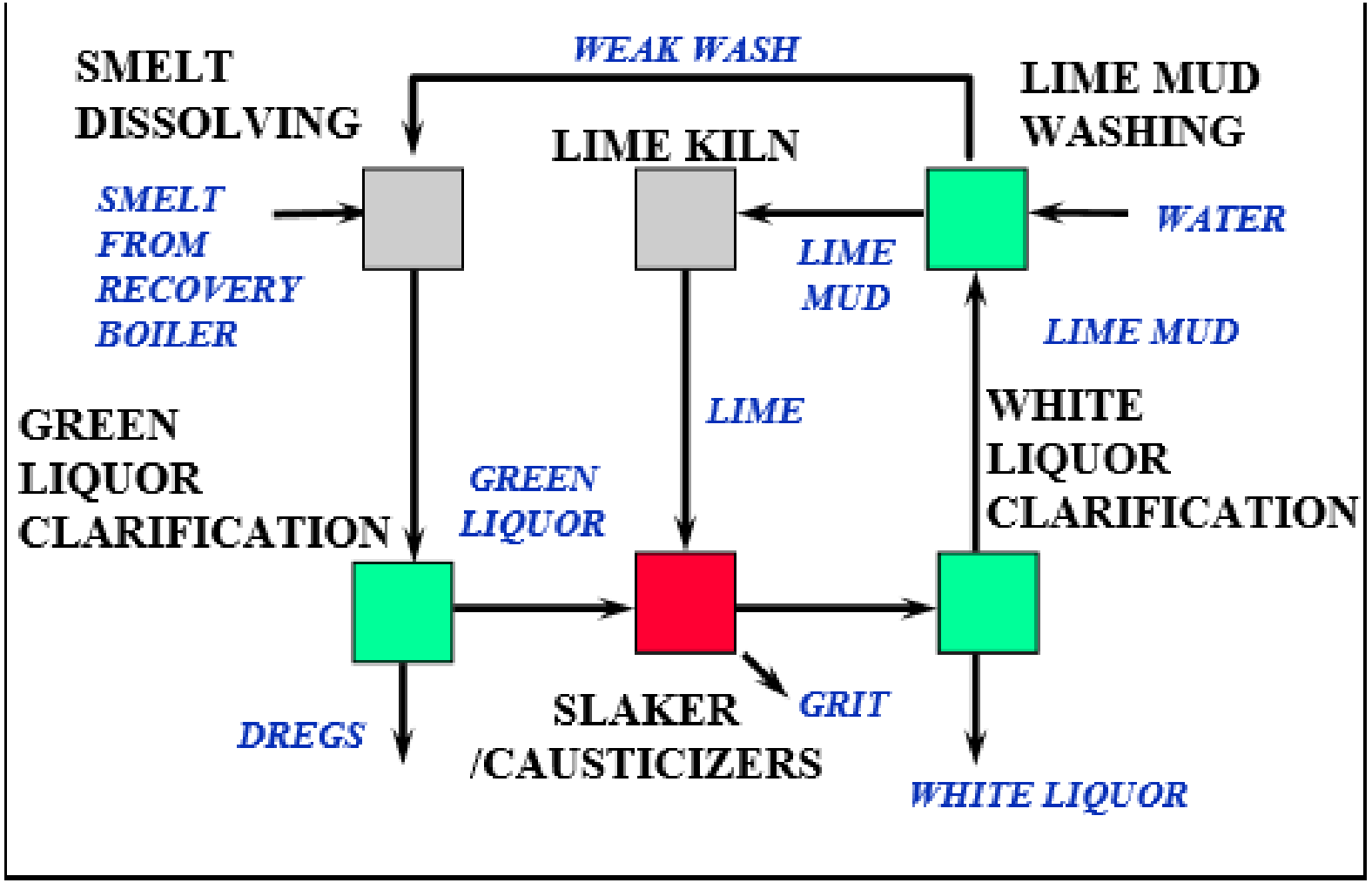
SULFIDITY %

Na_2S / AA or Na_2S / ($NaOH$+Na_2S)

CE = CAUSTICIZING EFFICIENCY %

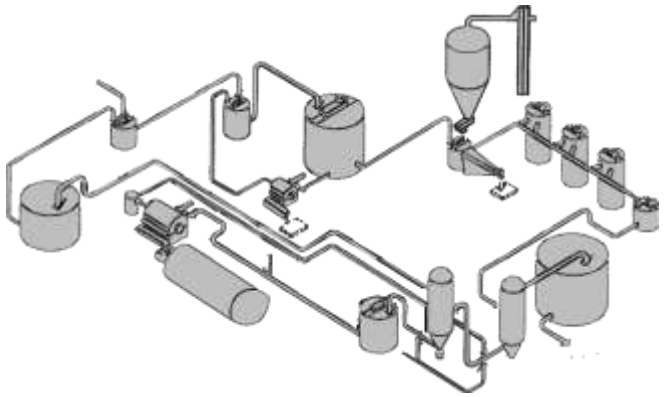
$NaOH$ /($NaOH + Na_2CO_3$)

Basic flow chart:



Recausticizing

- The three main processes that occur in recausticizing are:

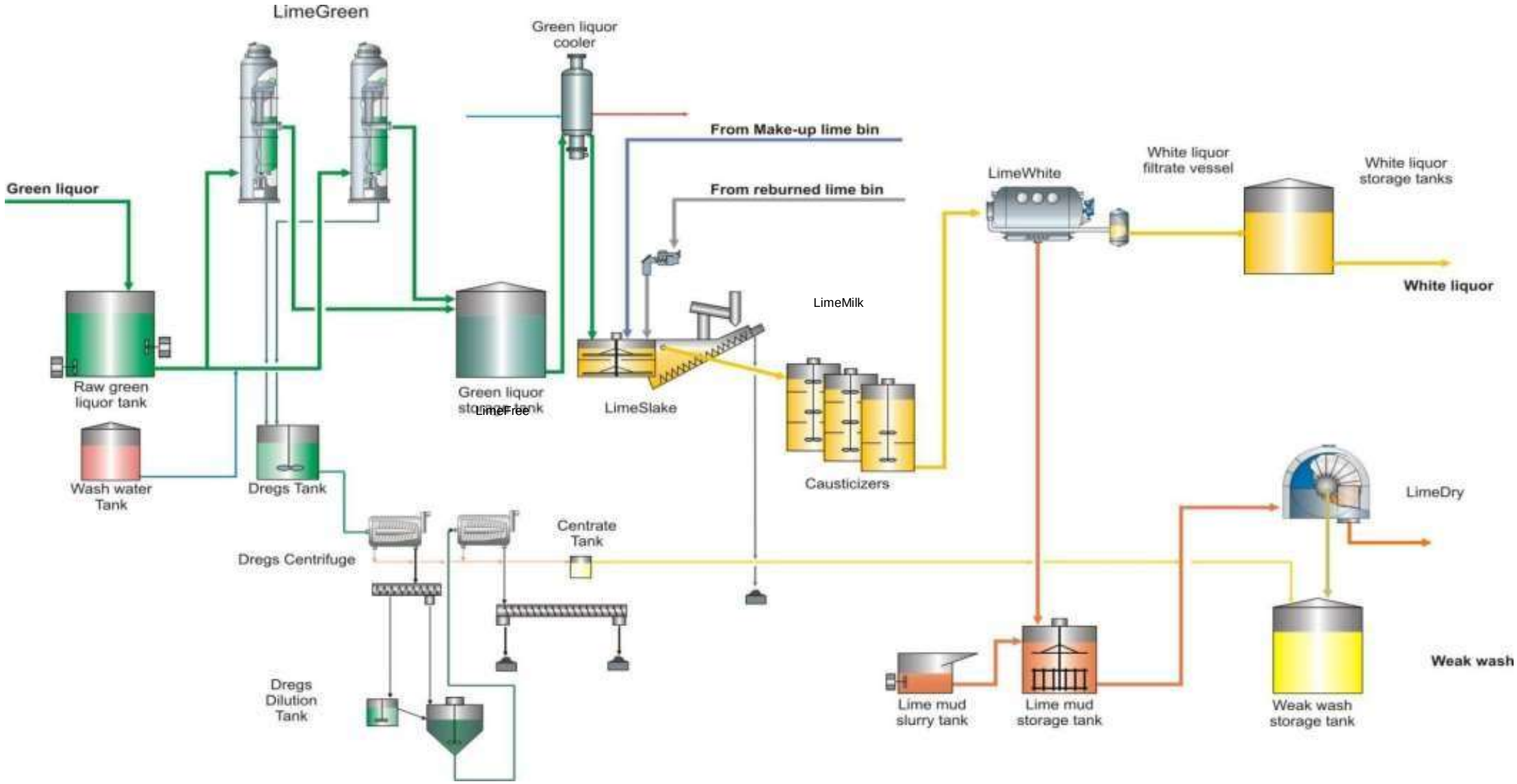


$CaO + H_2O \rightarrow Ca(OH)_2$

$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$

solids in liquor $\rightarrow$ solids + liquor

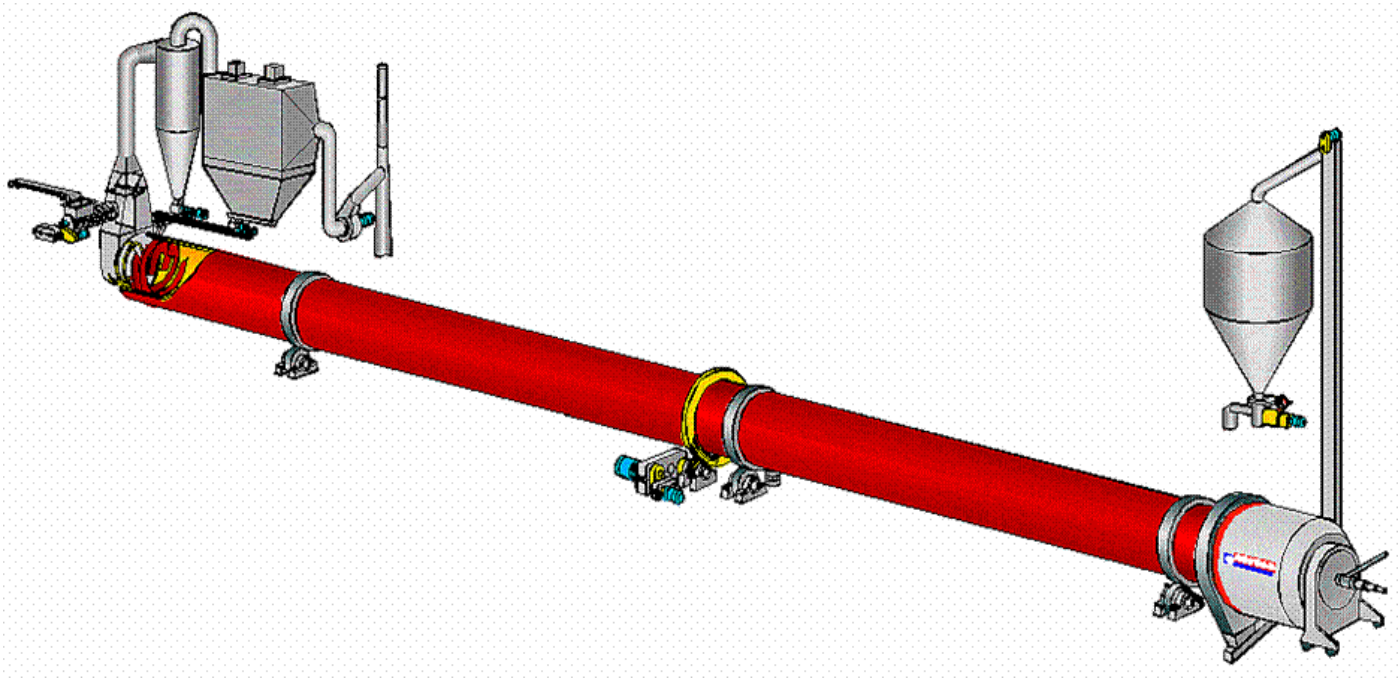
Recausticizing Process



Causticizing in modern mill

• White liquor active alkali (NaOH)	g/l	136
• White liquor sulfidity	%	32
• Causticity	%	82
• Reduction efficiency	%	95
• Green liquor filtration		
• White liquor filtration		
• Capacity	m^3WL/d	>10 000

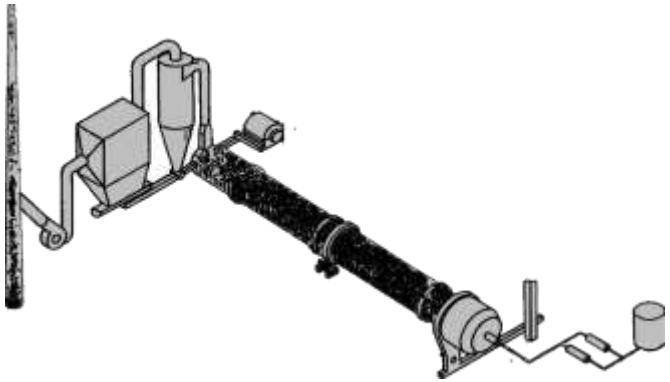
Lime kiln



Mission – Converting used lime mud into lime

Lime kiln

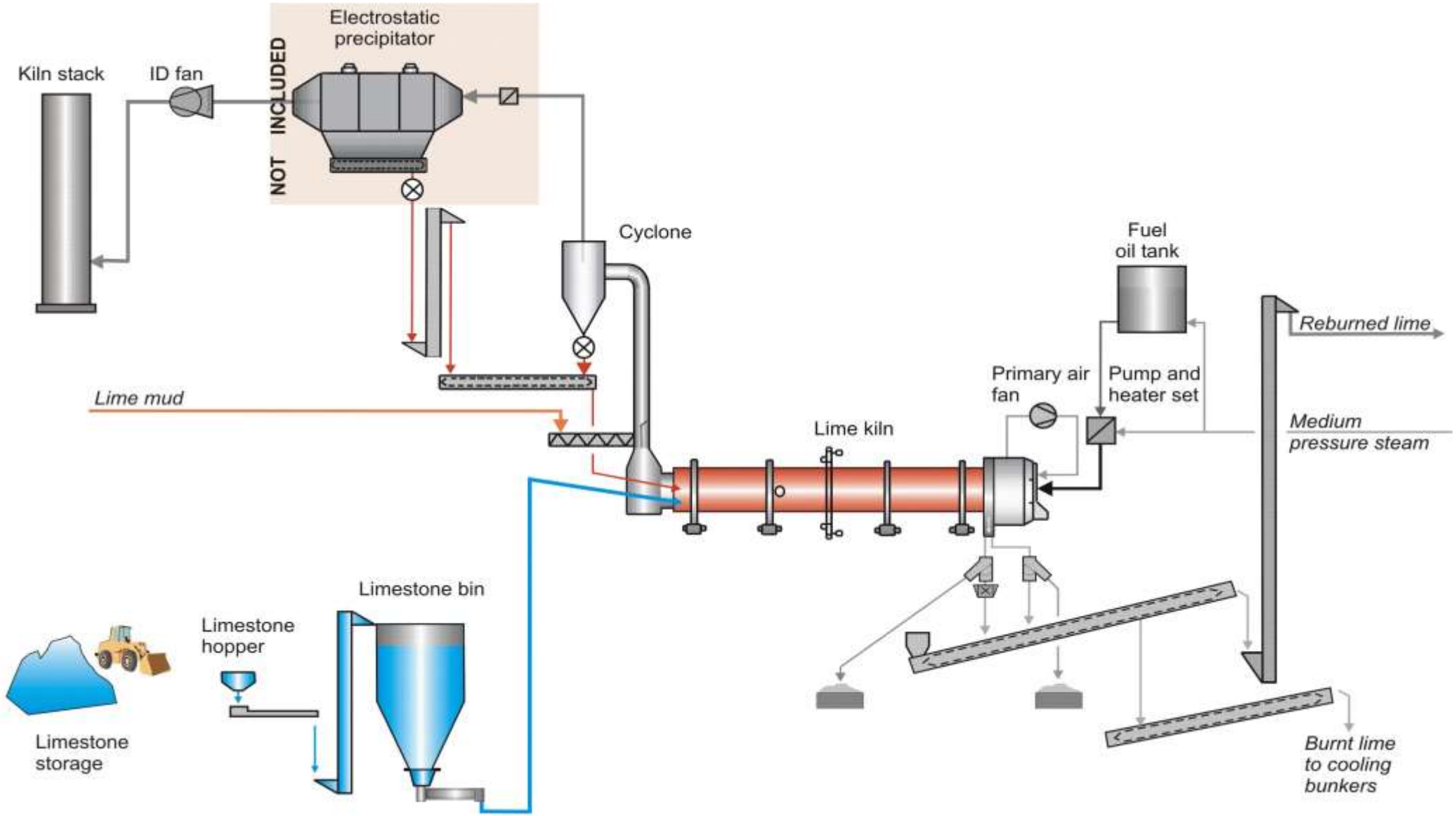
- The main processes that occur in lime kiln are:



Lime mud + Heat → **$CaCO_3$ + vapor**

$CaCO_3$ + Heat → **CaO + CO_2**

Lime kiln Process Flow

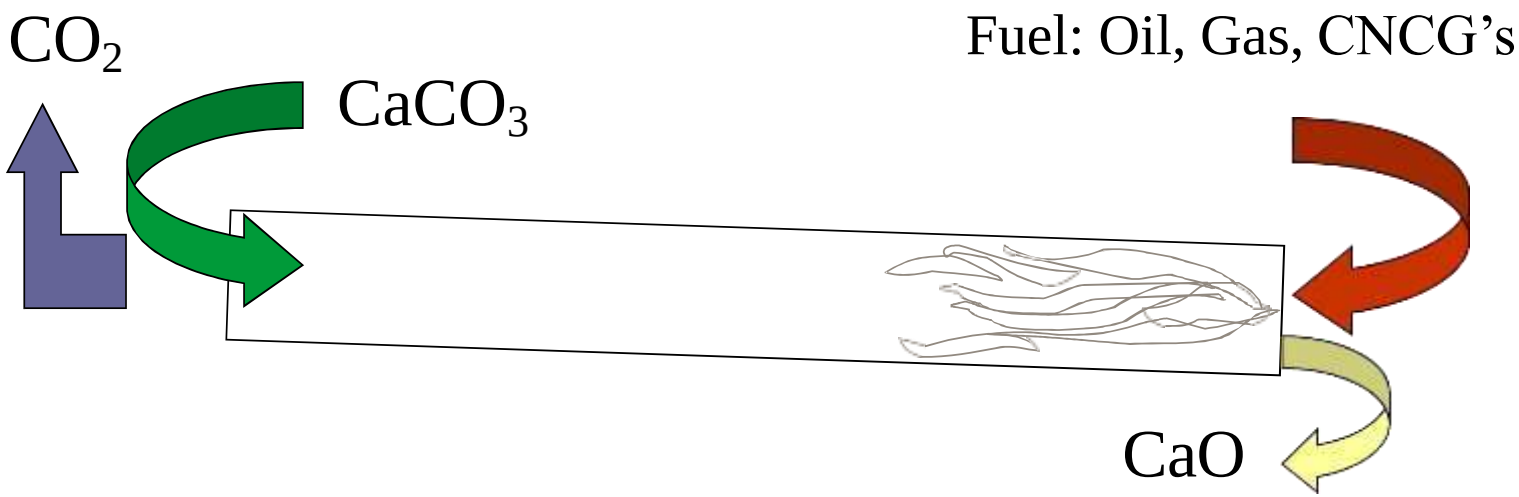


Lime kiln fuels

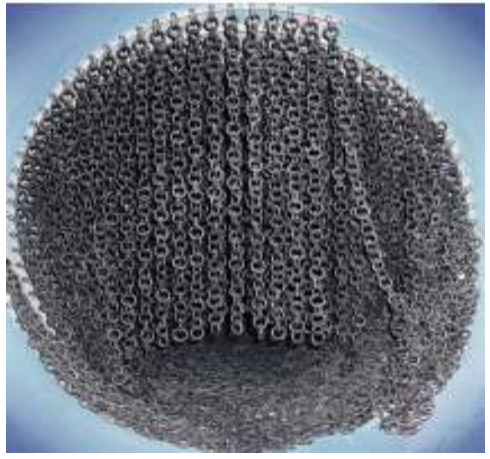
- Natural gas
- Fuel oil
- NCG’s
- Methanol
- Gasification gas
- Saw dust
- Pet coke

Lime kiln

- Lime mud + heat → burned lime + carbon dioxide
- Adiabatic flame temperature 1750 °C



Chain section



Hanging type

Garland type

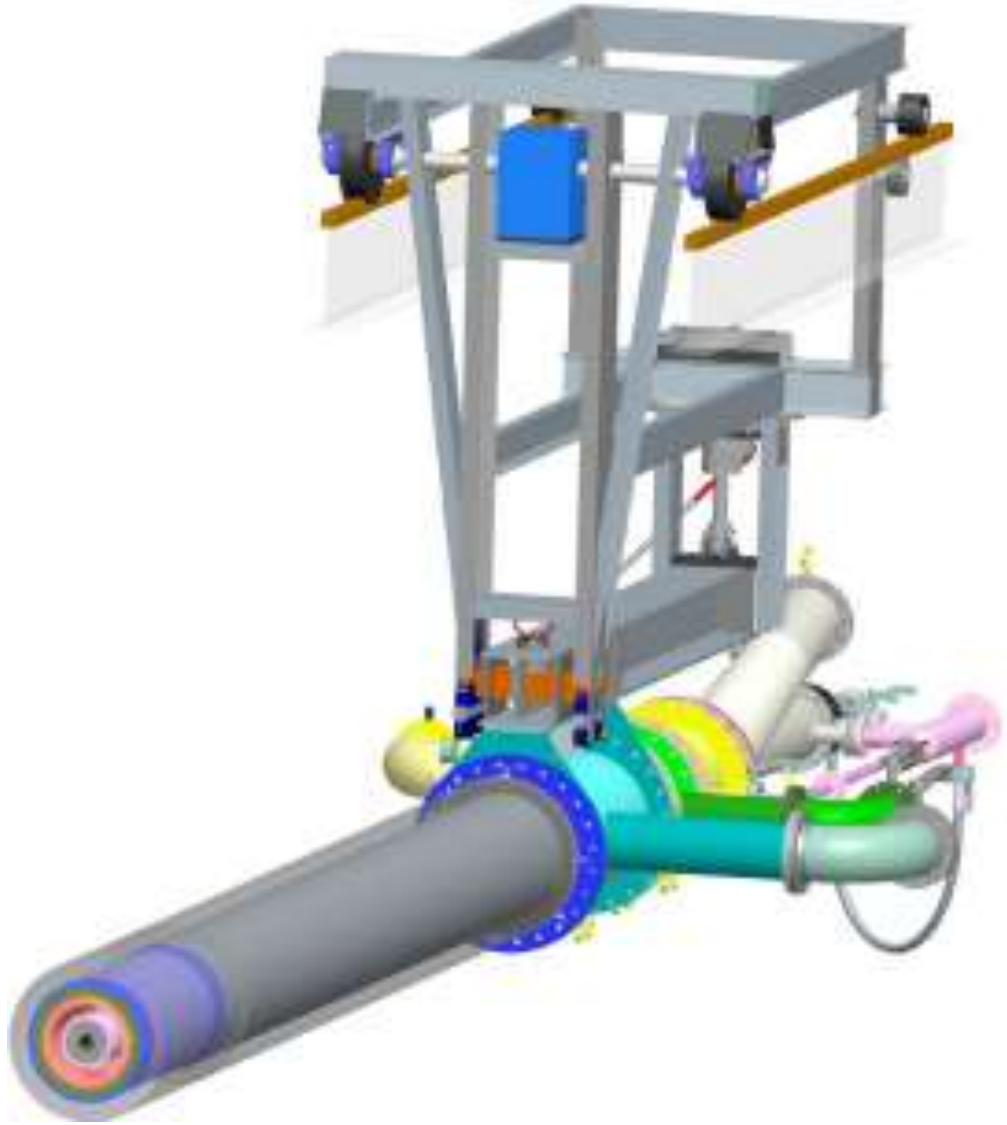
Satellite coolers

Multi fuel burner

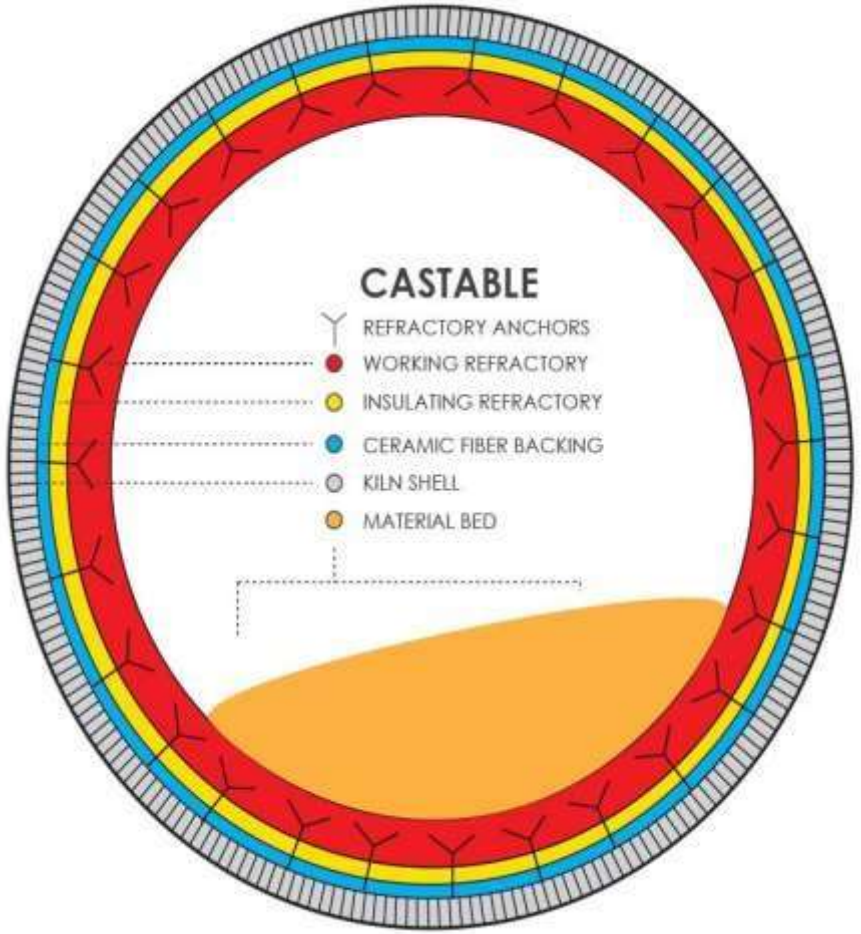
- Apart from Fuel Oil , burner designed to take fuels like Producer gas, Bio-gas, CNCG

- Flexible selection of mix of fuel combination

- Efficient combustion in joint development with burner Partner



Refractory inside kiln:



Critical parameters:

- Kiln feed end
- LMCD mud moisture
- Burning zone temperature
- O_2
- ID FAN SPEED
- Oil flow and temperature