

Lecture 3

**Recovery of Chemicals from
Kraft Pulping Process**

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RECOVERY OF CHEMICALS FROM KRAFT PULPING PROCESS

Chemical recovery system is an integral part of pulp and paper units and the efficiency of chemical recovery plays an important role in economics. Efficiency of chemical recovery units in terms of thermal efficiency, energy recovery and conversion of thermal energy to electrical energy has tremendous impact on overall economy of pulp production [Kulakarni, 2010]. Although earlier agro-based mills were not having recovery furnace due to high silica content of black liquor and smaller capacity, however now chemical recovery in agro-based mills have been made mandatory. Important terms in recovery of chemicals are given in Table M-III 3.1.

Table M-III 3.1: Important terms in Recovery of Chemicals

Active alkali	$\text{NaOH} + \text{Na}_2\text{S}$
Effective alkali	$\text{NaOH} + 1/2 \text{Na}_2\text{S}$
Total titratable alkal	$\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3$
Sulfidity	$\text{Na}_2\text{S} / \text{Titratable alkali}$
Causticity	$\text{NaOH} / \text{NaOH} + \text{Na}_2\text{S}$
Causticity Efficiency	$[\text{NaOH} / \text{NaOH} + \text{Na}_2\text{S}] \times 100$
Reduction	$\text{Na}_2\text{S} / (\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S})$
Over all recovery	Recovery = black liquor stock/ fresh liquor consumed

KRAFT RECOVERY

Recovery of chemicals from black liquor is very important for overall economy of paper industry. Kraft recovery process flow diagram is shown in Figure M-III 3.1. Various sections in kraft recovery plant are

- Evaporation section and further concentration: Multiple effect evaporator, direct contact, cascade evaporator, Cyclone evaporator, venture scrubber
- Recovery furnace: Furnace, ESP [Figure M-III 3.2]
- Dissolving Tank and Green liquor generation
- Causticizing and clarification
- Lime sludge reburning

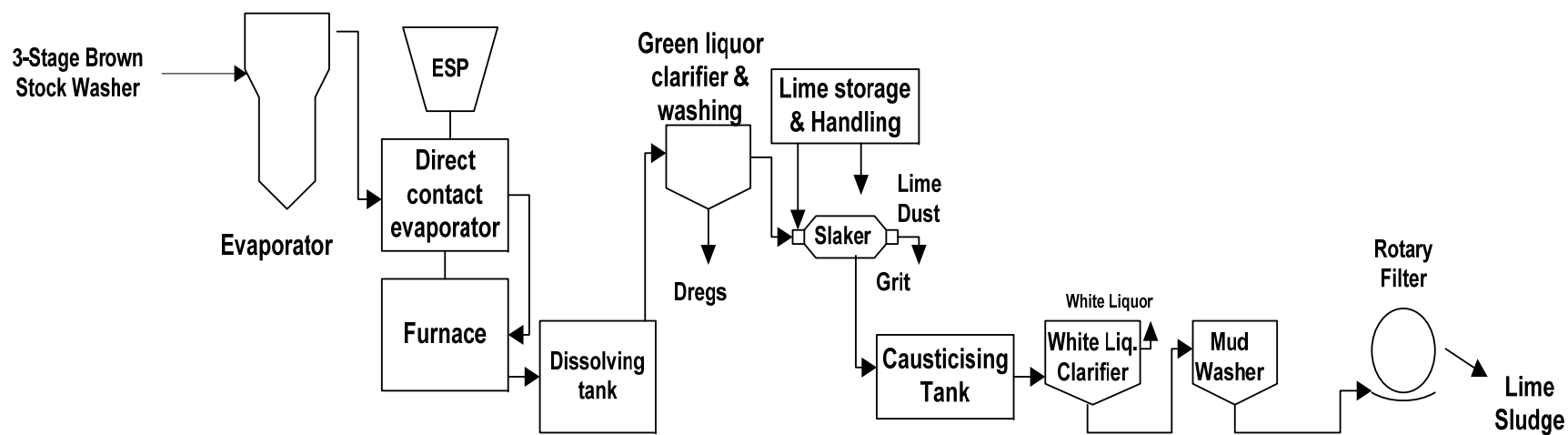


Figure M-III 3.1: Kraft Recovery Process

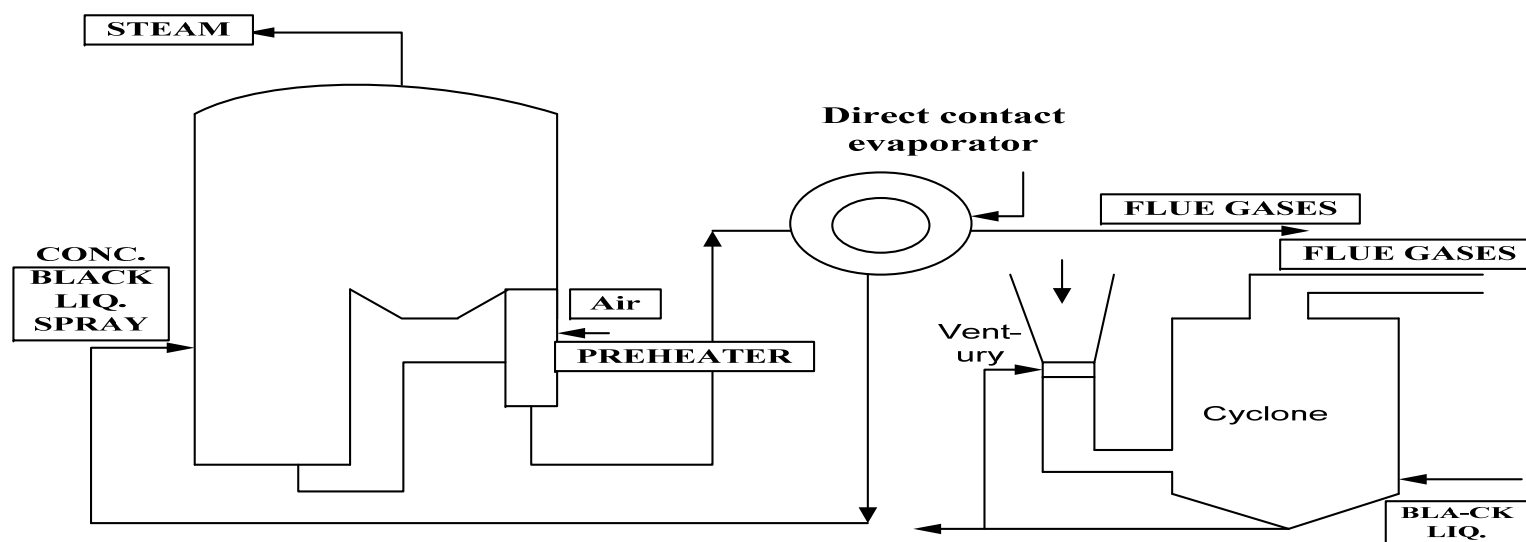


Figure M-III 3.2: Kraft Recovery Furnace

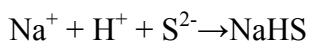
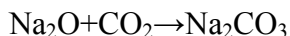
Black Liquor Oxidation: Black liquor oxidation has become integral part of recovery section for reducing the emission of volatile sulphur compounds. Oxidation of black liquor by air reduces the emission of odorous sulphur compounds. Mercaptans and other sulphur compounds are oxidized into less volatile chemicals. Both weak black liquor and concentrated black liquor oxidation has been reported. Typical Composition of Black Liquor from Wheat Straw Pulping is given in [Table M-III 3.2](#).

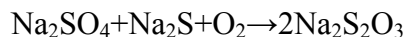
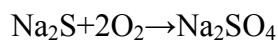
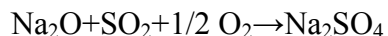
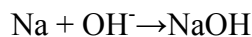
Various steps involved in kraft recovery section are

- Concentration of black liquor with inlet 12-18 percent and outlet 40-50 percent long tube evaporator. Normally five to six effect evaporator is used. As the black liquor become highly viscous, further concentration is done by direct contact evaporator and falling film evaporator
- Further concentration in direct contact evaporator to 60%. Using cyclone evaporator, cascade evaporator and venturi scrubber. In some of the mill Falling film evaporator is being used to achieve higher concentration of black liquor which is not possible with conventional evaporator. Other
- The concentrated black liquor is sprayed in the furnace where black liquor is incinerated to yield smelt and flue gases. A typical recovery furnace consists of air preheater, economizer, furnace and boiler, cyclone, venturi scrubber/ electrostatic precipitator.
- Addition of makeup chemicals Na_2SO_4 (salt cake) in thick concentrated black liquor which is reduced to Na_2S in the furnace in presence of carbon
- Incineration of Black Liquor in recovery furnace
- Reducing zone in bottom to burn organic
- Dying zone
- Oxidation zone

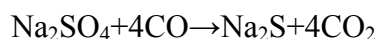
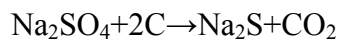
Reactions in recovery of chemicals from black liquor

The main reactions are (1-3 predominantly)

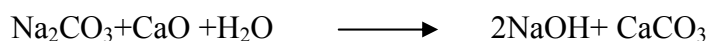




and other reactions:



- Dissolving smelt in dilute wash liquor or water to produce green liquor. Containing sodium carbonate and sodium sulphide.
- Causticising of green liquor with lime to produce white liquor, lime sludge. A typical causticising section consist of lime slaking with green liquor, dreg clarifier, causticising tank, clarifiers, rotary filter, lime kiln.



- Burning of lime sludge to produce lime.



Table M-III 3.2: Typical Composition of Black Liquor from Wheat Straw Pulping

Parameters	Wheat straw Black liquor
Total solids	10.8
Swelling volume ratio ml/g	10
Gross calorific value	2890
Silica as SiO ₂ %, w/w	2.87
Acid insoluble as SiO ₂ %, w/w	3.0
Chloride as Cl, %, w/w	4.3
Potassium as K, %w/w	6.0
Sodium as Na%, w/w	15.0
Calcium as Ca %, w/w	0.08

Inorganic as NaOH%, w/w	35.01
Organics%, w/w	64.99

Typical Characteristics of Black liquor

1 ton of black liquor - 2.2 ton of steam

Black liquor solid=1.30 ton /ton of pulp.

Weak black liquor per ton of pulp -10 -12 m³

Calorific value of black liquor: 3080 cal/gm

Black liquor-Organic 70%, Inorganic 30%

Weak black liquor: Na 28 gm/lit

RAA10.85 gm/lit

RECOVERY OF CHEMICALS IN AGRO-BASED MILL

With the shortage of forest based raw material and to preserve the forest, the paper industry in Asia and other parts of the world is forced to use non woody fibrous raw materials. India is one of the leading countries using substantial proportion of non wood materials which constitute about 50% of total raw material furnish [Dixit et al., 2012]. Non-wood raw materials are characterized by high silica content which varies from 1.5 to 20%. Most of the silica present in raw material passes into black liquor. Presence of silica in relatively high concentration creates numerous problems in chemical recovery plants. [Dixit et al., 2010]. Evaporator, recovery furnace, and lime kiln operation are adversely affected by presence of silica in black liquor [Ibrahim,1988].The process of distillation of bamboo and straw black liquors by carbonation has been developed by central Pulp and paper Research institute, Saharanpur,

Due to high silica content of the agricultural residues recovery of chemical from agro-based mills have caused major concern in Indian paper mills. Table M-III 3.3 gives the details of processes for recovery of chemicals from agricultural residues black liquor. Black liquor from cooking agricultural residues has high silica content and cannot be concentrated to high solid contents to enable its burning in conventional recovery

systems. Although, technologies are available and being practiced in many mills in other part of world; however, due to poor infrastructure still recovery of chemicals is not being practiced by majority of mills in Indian posing serious environmental pollution problems. Pollution load in agro-based small mills having no chemical recovery is almost three times to that of pollution load in large integrated mills

Some of the currently accepted technologies for recovery of chemicals for agro-based black liquor are: Rotary roaster, Roaster cum smelter, Broby smelter, Dry pyrolysis Process, Wet air oxidation process, Copeland reactor. Some of the emerging technologies are Wet cracking process, Chemsec process, Thermo chemical conversion reactor system, Super critical wet oxidation process, Direct causticization process, ABC process, Direct alkali recovery system (DARS) or Ferrite process. In the fluidized bed soda recovery system where the weak black liquor containing high silica content is concentrated to about 45percent concentration in multiple effect evaporator, venturi scrubber and cyclone system and is sprayed in the fluidized bed combustion system.

Table M-III 3.3: Processes for Recovery of Chemicals from Agricultural Residues Black liquor

Process	Description
Ferrite process (DARS process)	30% conc. Black liquor burnt with ferric oxide at temp 850 °c. $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{NaFeO}_3 + \text{CO}_2$ $2\text{NaFeO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{Fe}_2\text{O}_3$
Wet air oxidation process	Oxidation of organic matter at high temp 320-320 °c pressure 175-250 kg/cm ² .
Ultra Filtration and reverse osmosis	Sodium compound is removed as permeate. High molecules weight lignin fraction is rejected in interface.
COPE LAND process	34-35% Solid liquor is burnt in fluidized bed reactor. 650-

	700°C.
BKMI Process	Evaporation 35-37% in evaporator. Last two effect falling film. Upto 50% in direct contact evaporator, then concentrated black liquor is burnt.
Smelter cyclone evaporator	18-20% evaporation in multiple effect evaporator upto 50% inn cyclone evaporators. Concentrated black liquor is fired in furnace.
Destomax recovery system	Similar to Smelter cyclone process
Burning of Black liquor after desalination	Removal of silica by carbonation followed by concentration and burning

References:

1. Dixit, A.K., Jain, R.K., Mathur, R.M., “Incineration of black liquor mixed with waste biomass-An option to achieve zero black liquor discharge in small agro based paper mills” volume 245, No.3, 2012, p.161
2. Dixit, A.K., Thapliyal, B.P., Jain, R.K., Mathur, R.M., “Desilication of Bamboo & straw black liquor” IPPTA, Vol 22, No.3, 2010, p.121
3. Ibrahim, H. “Proceedings of the International non-wood pulping and paper making” Beijing, Vol II, 1988 p.877.
4. Kulkarni, A.G. “Removal of non-process elements in chemical recovery-A review technologies” Ippta, Vol. 22,No3.3, 2010, p.113