Chemical recovery

1 Overview of kraft recovery
Washing separates spent cooking chemicals and dissolved organics from pulp. The initial procedure was to discard this black, alkaline liquor. Chemical recovery systems were available, but their use did not become widespread until the 1930s and 1940s with the modern regeneration of spent liquor. Development of new equipment and an increase in mill size made it more economical to process black liquor than to buy new chemicals.

Recovery of black liquor has several advantages. Incineration of concentrated black liquor releases energy to generate steam and electricity. Regeneration of energy in contemporary mills exceeds internal needs. Mills therefore produce excess energy from their own waste.

1.1 Kraft recovery unit operations
Figure 1 shows the principal unit operations of the kraft recovery process:
- Evaporation of black liquor
- Combustion of black liquor in a recovery furnace to form sodium sulfide and sodium carbonate
- Causticizing sodium carbonate to sodium hydroxide
- Regeneration of lime mud in a lime kiln.

![Diagram of Kraft recovery cycles](image-url)
Other minor operations ensure the continuous operation of the recovery cycle. Removal of soap in the black liquor produces tall oil. Adding makeup chemicals such as sodium sulfate or sodium carbonate to a mixing tank or removing recovery boiler fly ash controls the balance of sodium to sulfur. Disposal of dregs and grits prevents accumulation of nonprocess compounds. Combustion processes odorous gases. Most modern or closed cycle mills use chlorine and potassium removal processes. With additional closure, internal chemical manufacturing methods are sometimes necessary.

1.1.1 Evaporation

The aim of evaporation is to produce black liquor of sufficiently high concentration with minimum chemical losses. Washing separates pulp and black liquor. The resulting weak black liquor contains 12%–20% organic and inorganic solids. Figures 2 and 3 show that burning this weak black liquor would require more heat than it would produce. The black liquor must therefore undergo concentration for efficient energy recovery.

The evaporation of black liquor in Fig. 4 has three principal unit operations:

- Separation of water from black liquor to generate concentrated black liquor and condensate
- Processing of condensate to segregate clean and fouled condensate fraction
- Separation of soap from black liquor.
A liquor processing stage such as a liquor heat treatment (LHT) unit can also be present to decrease black liquor viscosity. Another possible component could be a black liquor oxidation stage to decrease total reduced sulfur (TRS) emissions. In modern high solids evaporators, the mixing of recovery boiler electrostatic precipitator (ESP) ash occurs with 30%-45% dry solids black liquor. Non-condensable gases from evaporation require collection for processing. When using a direct contact evaporator stage, efficient oxidation of black liquor is necessary to suppress release of odorous gases into the flue gas stream.

Evaporation of black liquor uses direct or indirect heating and flashing of black liquor. Most industrial evaporators are the multiple effect, steam heated type. Vapor recompression evaporation is often a component in the first stage of evaporation of weak black liquor as a capacity booster.

Small mills use direct contact evaporation especially when processing nonwood black liquors. Hot flue gas from the recovery boiler heats a film or spray of black liquor. This technique can only evaporate to a maximum 65% dry solids content due to the steeply increasing liquor viscosity at higher dry solids contents. Unoxidized black liquor releases organic sulfur compounds on contact with flue gases. Oxidation of weak black liquor can partly avoid this. Economics favor the installation of indirect heating as unit size increases. Then all flue gas heat generates steam and electricity.

1.1.2 Recovery boiler
Concentrated black liquor contains organic dissolved wood residues and inorganic cooking chemicals. Combustion of the organic portion of liquor produces heat. In the recovery boiler, heat produces high pressure steam that generates electricity and low pressure steam for process use.

Combustion in the recovery furnace needs careful control. High concentration of sulfur requires optimum process conditions to avoid production of sulfur dioxide and reduced sulfur gas emissions. Besides
environmentally clean combustion, efficient reduction of inorganic sulfur must occur in char bed.

The process of the recovery boiler in Fig. 5 includes several unit processes:
- Combustion of organic material in black liquor to generate steam
- Reduction of inorganic sulfur compounds to sodium sulfide
- Production of molten inorganic flow consisting primarily of sodium carbon and sodium sulfide
- Recovery of inorganic dust from flue gas
- Production of a sodium fume to capture combustion residues of released organic sulfur compounds.

1.1.3 Lime kiln

A lime kiln calcines lime mud to reactive lime (CaO) by drying and subsequent heating. Fig. 6 shows. The calcining process can use a rotary furnace or a fluidized bed reactor. The main unit processes of the lime kiln are the following:
- Drying of lime mud
- Calcining of calcium carbonate

Some additional operations can also be present. The lime kiln combests small amounts of odoriferous noncondensible gases. The lime kiln process produces dust that requires capture. For larger amounts of oxidized sulfur gases, flue gas scrubbers are necessary.

The drying of lime mud and the calcining of calcium carbonate to calcium oxide require heat. This heat comes from burning oil or natural gas in the lime kiln. The lime kiln can also use other fuels such as gasified biomass.

1.1.4 Causticizing

The causticizing process in Fig. 7 converts sodium carbonate in green liquor to caustic soda.

The unit operations in causticizing include:
- Dissolving of molten smelt to weak white liquor to produce green liquor
- Green liquor clarification or filtration
- Mixing green liquor and lime in a slaker to form sodium hydroxide and lime mud with subsequent completion of the causticizing reaction in reaction tanks
- White liquor clarification and filtration for lime mud separation
- Lime mud washing.

Molten smelt from the recovery boiler contains small amounts of unreacted carbon and nonprocess elements. The small undissolved particles in green liquor require separation for disposal. Separation can use settling or filtration. Washing the dregs minimizes chemical losses.

1.2 Gasification
Gasification provides a way to convert solid fuel to a combustible gas. Use of combined cycle power generation where a gas turbine and a steam process produce electricity increases energy efficiency. Higher electricity conversion efficiency and high unit cost of the recovery boiler are the primary driving forces for development of new processes to replace recovery boilers.

Development of more efficient processes would offset the high unit cost of gasification. The recovery boiler has several weaknesses from an energy efficiency standpoint. The steam temperature and pressure are low, the energy of the smelt is not recovered, and the combustion temperature is low. Higher steam temperature and pressures could be possible if the product gas had proper cleaning. Recovery of energy of the smelt is possible if dissolving occurs under pressure. Higher combustion temperatures are possible when using oxygen instead of air in gasification.

From a process viewpoint, the recovery boiler also has several significant weaknesses. Recovery boiler downtime and accidents are expensive, and they limit pulp production. In reductive and oxidative processes, the possibility of smelt expansion and the corrosive process media cause high unit costs and require extra safety features. Although the modern recovery boiler is very environmentally friendly, new processes are under development to reduce emissions of NOx, SOx, and particles.

All the leading recovery boiler manufacturers are doing research on gasification. Several obstacles are hindering their progress. Energy conversion always entails extra losses. Cleaning gases is expensive. Reduction requires extra process equipment.

Table 1 shows that all commercial processes have less energy efficiency than conventional recovery boilers.
Table 1. Effectiveness of converting black liquor with high heating value (HHV) into fuel value in net product gas.

<table>
<thead>
<tr>
<th>Original HHV, MJ/tkgl</th>
<th>14.7 % of original</th>
<th>13.3 % of original</th>
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</thead>
<tbody>
<tr>
<td>Commercial processes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemrec (Kvarner)</td>
<td>55.9</td>
<td>50.7</td>
</tr>
<tr>
<td>StoneChem (MTCI)</td>
<td>49.0</td>
<td>42.6</td>
</tr>
<tr>
<td>Piloted processes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABB</td>
<td>70.4</td>
<td>66.6</td>
</tr>
<tr>
<td>Tampella</td>
<td>60.7</td>
<td>55.9</td>
</tr>
<tr>
<td>Conventional RB</td>
<td>61.1</td>
<td>58.6</td>
</tr>
</tbody>
</table>

A totally practical gasification process is still a long way from becoming commercially feasible.

1.3 Direct alkali recovery

Other processes can replace the conventional evaporator recovery boiler in the causticizing process of the lime kiln cycle. Because the number of new process stages is high and heavy investment is necessary, only few processes have evolved to the mill scale.

Australian Paper has processed liquor from soda pulping in a fluidized bed with ferric oxide. Water dissolves the resulting sodium ferrite to form sodium hydroxide and ferric oxides for recovery and re-use of the ferrous salt. The mill has accumulated several years of operational experience with this process.

The Fredericia mill used straw to make pulp for various applications. Despite the partially successful recovery operation, the mill closed because of other economic reasons.

The development of the Direct Alkali Recovery System (DARS) process is slow because using the fluidized bed with subsequent pelletizing and leaching operations are unfamiliar to typical pulp mill personnel.

2 Properties of kraft recovery process streams

Process calculations require property estimations of kraft recovery process streams. Individual operating practices, equipment differences, streams from bleaching chemical preparation, and fresh chemical makeup cause variations in process stream composition. When designing equipment or considering process changes, one should make every effort to measure all relevant property data. Solid fuel properties are given in Chapter 15.

2.1 Black liquor properties

Black liquor properties depend on the raw materials used for pulping, the pulping conditions, the equipment used for pulping, and the treatment of the liquor after pulping. The
argest supply of raw material for pulp production is definitely wood with a combination of softwood and hardwood finding frequent use. Interest in the use of other fibrous raw materials has revived. Mills in India, southeast Asia, and South America use bagasse, raw, reed, and bamboo.

The main variables in the conditions are the concentrations of the different chemicals in the cooking liquor, the chemical charge per weight of wood, the liquor-to-wood ratio, the cooking temperature, and the length of the cook.

Black liquor properties are not constant. They change as liquor flows from the digesters, pulp washing, evaporation, soap skimming, and storage. In optional processes, oxidation and liquor heat treatment have the greatest impact on liquor properties. Black liquor viscosity, boiling point rise, and heating value will especially vary.

1.1 Composition of black liquor

Black liquor contains water, organic residue from pulping, and inorganic cooking chemicals. The primary organic compounds are lignin, polysaccharides, carboxylic acids, and xylarcons. Table 2 gives a typical analysis of kraft black liquor.

<table>
<thead>
<tr>
<th>Organics, % by weight</th>
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<tbody>
<tr>
<td>Degraded lignin, including Na and S, %</td>
<td>37.5</td>
</tr>
<tr>
<td>Isosaccharinic acids, including Na, %</td>
<td>22.6</td>
</tr>
<tr>
<td>Aliphatic acids, including Na, %</td>
<td>14.4</td>
</tr>
<tr>
<td>Resin and fatty acids, including Na, %</td>
<td>0.5</td>
</tr>
<tr>
<td>Polysaccharides, %</td>
<td>3.0</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Inorganics, % by weight</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH, %</td>
<td>2.4</td>
</tr>
<tr>
<td>NaHS, %</td>
<td>3.6</td>
</tr>
<tr>
<td>Na₂CO₃ and K₂CO₃, %</td>
<td>9.2</td>
</tr>
<tr>
<td>Na₂SO₄, %</td>
<td>4.8</td>
</tr>
<tr>
<td>Na₂S₂O₃, Na₂SO₃ and Na₂Sₓ, %</td>
<td>0.5</td>
</tr>
<tr>
<td>NaCl, %</td>
<td>0.5</td>
</tr>
<tr>
<td>Nonprocess elements (Si, Ca, Fe, Mn, Mg, etc.), %</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The proximate analysis of black liquor determines the main components necessary for combustion calculations. It is used in typical mill recovery boiler calculations. Evaporator evaluations need boiling point rise and viscosity.

Proximate analysis usually consists of HHV, dry solids content of black liquor, inorganic material in black liquor dry solids, the inert material in organics vs. inorganics, and the ratio of reactive to nonreactive portions in organics vs. inorganics.

The advantage of proximate analysis is that it is simple to perform. No complicated equipment is necessary. Proximate analysis can estimate black liquor ultimate analysis and combustion properties.