THE KRAFT CHEMICAL RECOVERY PROCESS

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ABSTRACT

The kraft chemical recovery process is a mature, effective technology that provides for recycling of the pulping chemicals, efficient generation of steam and electrical power from the fuel value of the black liquor, and effective disposal of dissolved wood substances. The process now faces significant challenges with respect to air emissions, effluent discharge, and the need for improved energy recovery and utilization. Means for dealing with these issues are available, but they can costly. New technology may result in significant energy benefits.

INTRODUCTION

The kraft process, which uses sodium hydroxide (NaOH) and sodium sulphide (Na₂S) to pulp wood, is the dominant pulping process in the pulp and paper industry. About 130 million tons/year of kraft pulp are produced globally, accounting for two-thirds of the world’s virgin pulp production and for over 90% of chemical pulp. The high strength of kraft pulp, the ability of the process to handle almost all species of softwood and hardwood, and the favourable economics due to high chemical recovery efficiency (about 97%) give the kraft process an advantage over other pulping processes.

In the kraft process, about half of the wood is dissolved, and together with the spent pulping chemicals, forms a liquid stream called weak black liquor (Figure 1). The weak black liquor is separated from the pulp by washing, and is sent to the kraft recovery system, where the inorganic pulping chemicals are recovered for reuse, while the dissolved organics are used as a fuel to make steam and power.

For every ton of pulp produced, the kraft pulping process produces about 10 tons of weak black liquor or about 1.5 tons of black liquor dry solids that need to be processed through the chemical recovery process. This paper discusses the basic steps in the kraft recovery process, problems encountered and challenges in recovery operation, and advanced technologies that have been developed to overcome the problems.

THE RECOVERY PROCESS

Figure 2 shows a simple flowsheet of the kraft chemical recovery process. The process has three main functions: i) minimizing the environmental impact of waste material (black liquor) from the pulping process; ii) recycling pulping chemicals, NaOH and Na₂S; and iii) co-generating steam and power.

The magnitude of the recovery process is often not fully appreciated. Globally over 1.3 billion tons per year of weak black liquor are processed; about 200 million tons per year of black liquor dry solids are burned in recovery boilers to recover 50 million tons of cooking chemicals as Na₂O, and to produce 700 million tons of high pressure steam. This makes black liquor the fifth most important fuel in the world, next to coal, oil, natural gas, and gasoline [1]. Since black liquor is derived from wood, it is the most important renewable bio-fuel, particularly in Sweden and Finland.

The chemical, physical and combustion properties of black liquor vary from mill to mill depending on many factors, including mill location (inland or coastal), digester
conditions, pulp yield, wood species, white liquor properties, chemicals-to-wood ratio and brownstock washing efficiency. In general, hardwood pulping requires less chemicals, has a higher pulp yield, and consequently, generates less black liquor solids than softwood pulping. Hardwood black liquor generally contains less organics, tall oil and soap, and has a lower heating value (about 5% lower) than softwood black liquor. In Brazil, Chile and tropical countries, eucalyptus is the dominant wood species used in kraft pulping. Since the properties of eucalyptus black liquor are similar to those of other types of hardwood black liquor, the chemical recovery process in eucalyptus kraft mills is essentially the same as others.

Recovery of Pulping Chemicals, NaOH and Na₂S

As shown in Figure 2, weak black liquor from brown stock washers is concentrated in multi-effect evaporators and concentrators to a point where it can be effectively burned in a recovery boiler, usually at 65% solids or higher. Concentrated black liquor is sprayed into the lower part of the recovery boiler where it is burned in an oxygen deficient environment so that Na₂S is formed. The extent of sulphide formation is measured by the reduction efficiency, typically over 90%. The inorganic sodium and sulphur are recovered as a molten smelt which consists mostly of Na₂S and sodium carbonate (Na₂CO₃). The molten smelt enters a dissolving tank where it is dissolved in water to form green liquor. The green liquor is then sent to the causticizing plant, where it is reacted with lime, CaO, to convert the Na₂CO₃ to NaOH. Conversion is measured by causticizing efficiency, typically 80 to 83%. The Na₂S passes through the causticizing step unchanged.

The causticized green liquor is known as “white liquor” which contains mostly NaOH and Na₂S. It is returned to the digester for reuse in pulping. The precipitated CaCO₃ (lime mud) from the causticizing reaction is washed, and sent to a lime kiln where it is heated to a high temperature to regenerate CaO for reuse.

Recovery of Heat from Combustion of Organics

The organic compounds in black liquor serve as a fuel for the production of steam which is used to generate electricity. The heat released as a result of black liquor combustion is recovered as high pressure/temperature superheated steam in the recovery boiler. The efficiency in converting the fuel value in kraft black liquor (13,000 to 15,000 kJ/kg) to steam is typically lower than for fossil fuel combustion, because of the heat used to evaporate the water entering with the black liquor, the heat of reaction consumed in producing Na₂S, and the heat carried out with the molten smelt.

The amount of steam produced is typically about 3.5 kg per kg black liquor solids, but can range from 2.5 to about 3.8 kg steam per kg black liquor solids, depending on the thermal efficiency of the recovery boiler. The high pressure steam is passed through a steam turbine to generate electricity. Depending on the quality of the steam, and the type of the turbine, a 1000 t/d kraft pulp mill can generate 25 to 35 MW of electricity by burning 1500 t/d black liquor dry solids in its recovery boiler. The lowered pressure steam exiting from the turbine is used in various processes in the mill.

OPERATIONAL PROBLEMS

Although the kraft recovery process is straightforward in principle, it is not easy to operate at high efficiency. Many problems, both mechanical and process, can occur.

Multi-effect evaporators often experience problems with liquor side fouling, tube corrosion and foaming, particularly as the liquor becomes concentrated. These problems result in frequent evaporator boilouts, high steam consumption, and low solids in the product liquor. Recovery boilers also have many problems including fouling of heat transfer tubes and plugging of flue gas passages by fireside deposits, tube corrosion and cracking, floor tube damage, poor water circulation, smelt-water explosions, unsteady smelt run-off, high dregs in smelt, poor smelt reduction, low steam production, blackouts and air emissions.

Many problems can also occur in lime kilns including: low thermal efficiency, high fuel consumption, ringing, balling, dusting, refractory and chain damage, poor lime quality and air emissions. In the causticizing plant, problems often encountered are overliming, poor mud settling and washing efficiency, high sodium and low solids contents in the lime mud, low liquor causticizing efficiency, high dregs carryover and liquor-line corrosion in storage tanks.

Depending on the performance of the recovery boiler and the causticizing plant, and the amount and the way in which makeup chemicals are added into the system, the liquor cycle may have problems with non process element accumulation, particularly chloride (Cl) and potassium (K), with high Na₂CO₃ and Na₂SO₄ deadload, and with Na and S imbalance.

These operational problems result in poor pulping liquor quality, poor pulp quality, increased mill energy consumption, and decreased mill production capacity. They also make it difficult for mills to comply with increasingly stringent environmental regulations, particularly during the process disturbance periods.
EVIRONMENTAL CHALLENGES

Air Emissions

One of the key environmental challenges is control of air emissions from the recovery cycle. The main concerns have historically been particulate, TRS (total reduced sulphur gases, mainly H₂S), SO₂, and recently NOₓ. Now, there is increasing focus on other gases, such as HCl, NH₃, CO, methanol, and other volatile organic compounds.

Particulate emissions are mainly from the recovery boiler, the smelt dissolving tank and the lime kiln. Modern recovery boilers are equipped with sectionalized, dry-bottom electrostatic precipitators that operate at high efficiencies (>99.5%). Smelt dissolving tank vent stacks are equipped with high efficiency wet scrubbers to control particulate emissions. Lime kilns are equipped with either wet scrubbers or precipitators to control lime dust and sodium fume emissions. Although wet scrubbers have the advantage of also providing some capability to control SO₂ emissions, virtually all new lime kilns are equipped with electrostatic precipitators to meet tighter particulate control requirements.

TRS is primarily responsible for kraft odour and has long been subject to control measures. TRS emissions from modern recovery boilers are kept well below 5 ppm. Other main sources of TRS emissions are non-condensible gases (NCG) streams from the digesters and evaporators. They are normally collected and incinerated either in bark boilers, dedicated incinerators, lime kilns, or recovery boilers. There has been increased trend toward burning NCG in recovery boilers [2], which are adequate from both process and capacity standpoints and have the advantage of a built-in means for capturing the sulphur.

SO₂ emissions can also come from many sources. Recovery boiler SO₂ emissions depend strongly on boiler operating conditions. The SO₂ concentration in the flue gas can approach zero if the temperature in the lower furnace is sufficiently high. SO₂ emissions from the lime kiln are dependent on the sulphur content of the fuel being burned and on whether or not the calciner is being used for NCG incineration. If wet scrubbers are used for capturing lime dust, some SO₂ recovery will also occur there. The emission of SO₂ from bark and power boilers depends on the sulphur content of the fuel used and on the efficiency of any wet scrubbers that might be employed. SO₂ emissions from NCG incinerators depend on scrubber efficiency.

NOₓ emissions from recovery boilers are relatively low, typically 50 to 100 ppm. Most of this NOₓ comes from the small amount of nitrogen compounds (0.1 wt%) in the black liquor solids burned in the boiler [3,4]. At present, it is not clear if NOₓ emissions can be controlled through changes in boiler operating practices. NOₓ emissions from lime kilns have recently attracted attention, particularly for kilns that burn NCG.

Combustion control in modern recovery boilers is quite good, and CO concentrations during normal operation are typically only a few hundred ppm. However, CO concentrations can be considerably higher during upset operation.

HCl can be emitted from the recovery boiler, as a result of sulphation of alkali chlorides (NaCl and KCl), if SO₂ concentrations are high and if there is sufficient chloride in the black liquor. Reductions in HCl emissions can be achieved by operating the recovery boiler with high bed temperatures to minimize SO₂ concentrations in the flue gas and by purging chloride from the system.

Small amounts of NH₃ and ammonium salts have been found in the dissolving tank vent [5]. This comes from organic nitrogen in the wood that is dissolved during pulping and ends up in the smelt stream leaving the recovery boiler. The nature of this problem and how to minimize it is only now beginning to be understood [4].

Methanol and other volatile organic compounds are formed during pulping and can be present in contaminated condensates. They can be stripped out using condensate strippers, and can be dealt with as a part of NCG and stripper-off-gas (SOG) incineration, or they can be incinerated as liquids. In older recovery boilers, these substances also form during black liquor oxidation and can be stripped from the black liquor in direct contact evaporators. The need to control these emissions may eventually result in the total elimination of the use of direct contact evaporators.

Mill Closure

The second major environmental challenge for the kraft process is how to reuse various aqueous effluents within the pulp mill. This challenge, which is often referred to as mill closure, is aimed at decreasing the overall water usage and the needs for chemical makeup.

Steam condensate is used where possible instead of fresh water. This requires greater efforts to clean up condensates to make them suitable for reuse. Any organic substances that are present in contaminated condensates will be moved to parts of the system where they had not previously been present. This can have adverse effects on the process.

The decrease in chemical makeup requirement does not necessarily result in an economic benefit. It may force a
change from cheap chemicals (such as Na$_2$SO$_4$) toward more expensive ones (NaOH). For bleached kraft mills, spent chemicals (mostly Na$_2$SO$_4$) from chlorine dioxide (ClO$_2$) generators have been disposed of by introducing them into the recovery system as makeup chemicals. An ongoing trend toward a decreased need for sulphur makeup has forced changes in ClO$_2$ generation technology to produce an effluent having less sulphur. The need for less sulphur can also affect on-site acidulation of tall oil soap, since sulphuric acid is the acid normally used for this purpose. However, this is not a problem for eucalyptus or other types of hardwood mills where tall oil soap production is minimal.

Non-process elements (NPEs) are chemical elements that are present in the process cycle, other than the sodium and sulfur that make up the pulping chemicals and the carbon, hydrogen and oxygen that make up the organic material. NPEs can enter the cycle with the wood, with chemical makeup, with process water, from the bleach plant, and with any waste streams that are disposed of within the process. Non-process elements can be classified into three general types: i) those that are highly soluble in alkali and can build up without limit (K and Cl); ii) those that are partially soluble in alkali and can build up to significant levels before being naturally purged by precipitation (Al, Si, P), and iii) those that are highly insoluble in alkali and are removed with green liquor dregs and therefore do not build up (Ca, Mg, Ba, Fe).

Potassium (K) and chlorine (Cl) can have a large effect on the recovery operation, since they lower the melting points of the ash formed in the recovery boiler. Potassium is an active alkali, like sodium, and KOH and K$_2$S are effective pulping chemicals. In tightly closed mills, potassium may accumulate to more than 10% of the total alkali, especially when eucalyptus/hardwood is pulped. A high potassium level in the liquor aggravates superheater corrosion and increases fouling in the recovery boiler, particularly when it is also accompanied by a high chlorine (or chloride) level [6]. Chloride can have a major impact on recovery boiler fouling and plugging, and has been implicated in some corrosion problems around the system. As the degree of mill closure increases, deliberate purges for Cl and K from the recovery cycle may be required.

Al and Si can form glassy aluminosilicate scales in the evaporators, which are difficult to remove. The critical element for controlling this problem is normally Al, and Al inputs to the cycle should be minimized. If necessary, Al can be removed from the cycle with the green liquor dregs, by co-precipitating it with Mg. High levels of silica can result in evaporator scaling and lime mud filtering problems. Phosphorous will tend to build up in lime cycle and result in poor quality lime and operational problems in the lime kiln.

The alkaline insoluble NPEs such as Ca and Mg can cause scaling problems in digesters and evaporators, upstream of the green liquor dregs separator, but they do not accumulate in the cycle.

In recent years, there have been efforts to use the recovery system for disposal of biological sludge from the waste treatment system [7]. There are some concern about this practice since it increases the load on process equipment, and is also a potential source of non-process elements. Sludges that can contain significant levels of aluminium are especially troublesome.

**MODERN APPROACH**

The modern kraft recovery process is the end result of continued small improvements in the basic technology. One important development in recovery boiler operation is the “high-solids firing” which refers to burning black liquor at solids contents greater than 75%. The practice significantly increases steam generation and improves combustion stability, resulting in lower TRS and SO$_2$ emissions, and less boiler fouling and plugging. It also provides for more capacity in existing units.

The amount of power a recovery boiler can generate from black liquor combustion depends on the pressure and temperature of the steam that the boiler produces. Traditionally, recovery boilers have operated at moderate steam pressures (90 bars) and temperatures (<480°C) due to concerns over superheater corrosion and high costs of material construction. The trend is, however, toward higher pressures and temperatures. The lead in these developments has been taken in Japan and Finland. Today there are a number of recovery boilers operating at 110 bars and 510°C. Steam generation rates can be as high as 3.8 kg steam per kg black liquor solids (BLds) and power generation, as high as 0.6 kWh/kg BLds.

Figure 3 shows the firing capacity of over 1000 recovery boilers that have been built in the world to date [8]. While fewer units were built in the last decade compared to previous decades, the units are larger on average, with the maximum black liquor firing capacity double those built in the early 80’s. The boiler steam temperature and pressure are also higher (Figure 4) in order to allow for maximum power generation.
The largest recovery boiler in the world is presently the Kvaerner unit started up in November 2004 at the Jinhai Pulp & Paper mill in Hainan, China (Figure 5). The unit is sized at 16.4m x 16.4m x 65m (H), and has a nominal firing capacity of 5000 t/d BLds (6000 t/d BLds maximum) and producing 734,000 kg/hr steam rated at 84 bar and 480°C [9].

A state-of-the-art mill may have high-solids evaporators/concentrators to bring the liquor to 80-85% solids for firing in the recovery boiler. Figure 6 shows a schematic of the high dry solids evaporator by Andritz. It has much more heat surfaces than conventional evaporators. Due to the high viscosity of the black liquor at high solids contents, a LHT (Liquor Heat Treatment) system is used to lower the liquor viscosity and make it easy to process.

The recovery boiler design will be that of a single drum, high solids firing unit with multiple levels of air supplied by separate fans, as shown in Figure 7. It will have a greater superheater surface area and be equipped with feedwater preheaters and/or combustion air preheaters in order to produce high-pressure/temperature steam. It will also be equipped with a back pressure turbine combined with a condensing turbine to maximize power generation.
Sootblowers, which are used to control deposit accumulation on tube surfaces in recovery boilers, will be equipped with fully-expanded nozzles, variable lance speeds and intelligent blowing systems to maximize deposit removal efficiency while minimizing sootblowing steam usage. New recovery boilers will use low pressure steam after the steam turbine (10 to 15 bars) for sootblowing [10], instead of the conventional high pressure steam (20 to 24 bars).

The causticizing plant will incorporate slakers with cyclones and scrubbers to minimize dusting (Figure 8), pressurized disc filters instead of gravity settlers for liquid/solids separation (Figure 9). The calcining system will incorporate effective lime mud dewatering, a flash mud dryer, and product coolers (Figure 10) to improve kiln thermal efficiency.
Tightly controlled kraft mills will use some method for deliberate Cl and K removal. This might take the form of simply disposing of a substantial portion of the precipitator ash or the use of elaborate ash treatment systems for selectively removing Cl and K [11]. Complex systems for NCG collection and incineration will be universally used. These will handle not only the concentrated NCG streams, but also miscellaneous dilute NCG streams that contribute to mill odour, and will include destruction of malodorous gases collected from contaminated condensates. There will be increased pressures to use the recovery boiler to process at least a portion of the NCG load.

For bleached kraft mills, there will be increased incorporation of some of the process streams from the bleach plant into the recovery cycle. O₂-deliignification liquor will be disposed of in the recovery cycle. There will be increased incentives for bringing alkaline stage effluents back into the pulping cycle through countercurrent washing.

**FUTURE TRENDS**

**Gasification**

In recent years, black liquor gasification has received considerable attention as a potential replacement for recovery boilers. Black liquor gasifiers with this capability are still in the development stage and full-scale implementation is still years away. The driving force for these developments has been the potential for much greater electricity production if the gas produced can be burned in a gas turbine for combined-cycle power generation. However, many materials and gas clean-up issues remain to be resolved. Attention is now shifting to using black liquor gasification to produce synthesis gas as a raw material for making higher value chemicals for sale. This is sometimes referred to as the biorefinery concept.

**Borate Autocausticizing**

The process involves adding sodium borate into the liquor system so that it forms tri-sodium borate (Na₃BO₃) in the recovery boiler smelt [12]. Na₃BO₃ dissociates into sodium hydroxide (NaOH) and NaBO₂ in the dissolving tank. Thus, it is possible to causticize a portion of Na₂CO₃ in a recovery boiler with a small amount of borate, and complete the causticizing of the remaining Na₂CO₃ in the causticizing plant with a reduced amount of lime. Since no capital investment is required, partial autocausticizing is an attractive alternative for kraft mills where incremental causticizing and lime kiln capacity are needed.

Numerous mill trials have been conducted and problems encountered have been resolved. The technology is now being used at several mills in Sweden, Brazil, Indonesia and the United States. For a green-field kraft pulp mill, with proper equipment design and operation, the technology has the potential for completely eliminating the causticizing plant and the lime kiln, making the kraft process much simpler.

**Alternative Fuels for Lime Kilns**

The lime kiln is the biggest user of fossil fuels in the kraft process. With the escalation in costs of oil and natural gas, there has been considerable effort devoted to finding suitable alternative fuels for use in the kiln. These have included pet coke, gas from wood waste or bark gasifiers, and soap or tall oil. Methanol or other liquid fuels that may be obtained from NCG collection systems have also been considered.

**SUMMARY**

The chemical recovery process dictates the quality and quantity of the white liquor, which in turn, limits pulp production and the profitability of the kraft pulp mill. There are numerous ways in which the economics, energy efficiency, and environmental protection associated with the recovery process can be improved. Development of process sensors and control is an area undergoing rapid change. Much remains to be learned about the science of the kraft recovery cycle and about application of that science through improved processes and equipment.

With today’s increasingly high energy and chemical costs, and stringent environment regulations that limit particulate and gaseous emissions, solid waste disposal and mill effluent discharge, the need for improved recovery of energy and chemicals from the black liquor has become a critical economic factor in kraft pulp mill operation. It is essential for mills to maximize the steam and power production capacity, reduce recirculating chemical dead loads, and minimize chemical losses. The reliability and efficiency of recovery boilers, evaporators, causticizing plants and lime kilns have a direct impact on the quantity and quality of white liquor, and ultimately the quantity and quality of pulp produced by kraft mills.

The greatest opportunity for increasing energy and chemical recovery efficiency and for improving overall operating performance at existing kraft pulp mills is through advanced energy integration and mill-wide control. Although limited automatic control of the individual units that make up the process is available, there is presently no effective control strategy overseeing the entire cycle. Major disturbances, as well as chemical dead loads can propagate around and around the recovery cycle. Examples include changes in wood supply which will affect the black liquor heating value and boiler...
thermal efficiency, or in poor causticizing plant operation which will increase the carbonate deadload in the liquor cycle, leading to lower evaporator efficiency, lower black liquor solids content and poorer boiler reduction efficiency. With current technology, these changes are dealt with on an individual unit basis, when the performance of that piece of equipment begins to change.

Gains made in process understanding over the past years have reached a point where it is feasible to develop more comprehensive automatic control strategies and conceive of new and improved process designs.

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