



CHEMICAL RECOVERY IN KRAFT PULP MILLS: PROCESS OPTIMISATION AND RESOURCE RECOVERY

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ABSTRACT

Chemical recovery is a vital part of the Kraft pulp making process that recovers inorganic cooking chemicals and recovers energy from black liquor. The present study focuses on the evaluation of Kraft chemical-recovery cycle and optimization of the process and resource recovery. Representative baseline and optimised operating conditions were compared using the process-based analytical approach, for black-liquor evaporation, recovery-boiler operation, green-liquor clarification, causticization and lime regeneration. The key performance indicators were black-liquor solids, reduction efficiency, chemical-recovery efficiency, causticizing efficiency, lime availability, steam generation, energy consumption and inorganic-residue generation. The optimisation scenario suggested an increase in chemical and energy recovery, black-liquor solids, steam generation, reduction efficiency, causticizing performance and a decrease in supplementary fuel consumption, chemical losses and inorganic residues. The recovery of black-liquor energy, sodium chemicals, lime, process water, waste heat and inorganic residues were also considered. Integrated process optimisation is highlighted as a potential to increase the efficiency and sustainability of Kraft pulp mills.

Keywords: Kraft Pulping, Chemical Recovery, Black Liquor, Recovery Boiler, Causticization, Resource Recovery.

1. INTRODUCTION

One of the most widely used chemical pulping processes to make chemical pulp is the kraft process. In this process the wood chips are cooked with alkaline white liquor, which is a mixture of principally sodium hydroxide (NaOH) and sodium sulphide (Na₂S). Lignin and some hemicellulose dissolves during cooking and creates a spent cooking liquor called black liquor. The recovery of black liquor is therefore significant in order to reduce the use of chemicals, optimize energy use and ensure the economic and

environmental performance of the pulp mill, because it is not only organic, but also contains inorganic compounds, including sodium compounds.

The chemical recovery process is an ongoing cycle that consists of continuous evaporation of black liquor and continuous burning of black liquor in a recovery boiler. The amount of organic fraction is used to produce energy, and the inorganic fraction is recovered as smelt consisting primarily of sodium carbonate (Na_2CO_3) and sodium sulphide (Na_2S). The smelt is dissolved to produce green liquor which is then clarified and causticized to produce white liquor. The calcium carbonate created in the causticization process is turned back into calcium oxide in the lime kiln and used in the recovery cycle. As a result, the recovery system not only regenerates the chemicals but also generates steam, recovery of lime, and decreases the number of chemical wastes.

Although designed to be integrated, there are inefficiencies resulting from poor evaporation, incomplete combustion, poor green-liquor clarification, inefficient causticization, lime-kiln instability, chemical losses, and retention of non-process elements. These can impact chemical recovery, energy consumption, and create extra inorganic residues. The scientific studies presented over the last years have, therefore, emphasized advanced process monitoring and enhanced recovery control, alternative use of black liquor, and recovery of lignin.

This study, therefore, examines the Kraft chemical-recovery cycle from an integrated process-optimisation point of view. Representative baseline and optimised operating conditions are compared to evaluate improvements in chemical recovery, energy consumption, causticization, lime regeneration, and resource recovery. It also takes into account the possibility of energy, chemical, water and inorganic material recovery in the pulp-mill system.

1.1. Objectives of the Study

The study was undertaken with the following objectives:

- To examine the major stages and chemical transformations involved in the Kraft chemical-recovery cycle.
- To evaluate the influence of key operating parameters on chemical, energy, and material recovery.
- To compare representative baseline and optimised operating conditions using selected performance indicators.
- To assess opportunities for recovery and reuse of energy, chemicals, water, and inorganic residues.

2. LITERATURE REVIEW

Trung et al. (2015) explored the role of new analytical systems to enhance control in pulp-mill processes, such as chemical recovery. They pointed out that process variability in manufacturing and process efficiency in the operation can be reduced by accurate and continuous measurement of process variables. Advanced analysers and control strategies applied to the digester, dissolving tank, slaker and final causticizing control are discussed. Improved measurement and control strategies led to decreased process variability along with estimated chemical savings and reductions in the cost of energy. It is found that there is a need for reliable process monitoring and control to ensure stable and optimised chemical-recovery performance.

Magdeldin and Järvinen (2020) studied the energy and pulp-mill integration potential of supercritical water gasification of Kraft black liquor. They studied the conversion of weak black liquor into useful product gas by using process modelling, but with inorganic pulping chemicals being recovered. Through the analysis, the gasification system was shown to be able to achieve high energy efficiency from the aspect of co-production of gas, solid and hot water. The authors also proved that the system was capable of redirecting a part of the weak black liquor to the gasification system to increase the capacity of the pulp production without changing the energy requirements of the mill. Based on this study, it can be concluded that black liquor can be used as a fuel in a conventional recovery boiler and a potential feedstock for other resource and energy-recovery processes.

Argyropoulos et al. (2023) investigated the potential of Kraft lignin as a valuable and sustainable material other than combustion in the recovery boiler. The authors said Kraft lignin is mostly being used today for energy production and inorganic chemical recovery, with a potential added value in the separation of this lignin from black liquor. Lignin-separation technologies and potential applications were reviewed and the techno-economic and environmental issues of lignin valorisation were discussed. Importantly, lignin removal can decrease loads on the recovery boiler and possibly increase pulp production, and recovered lignin can be used as a fuel, chemical, or material feedstock. The concept of chemical recovery from simple combustion and chemical regeneration is extended in the present study towards wider biorefinery and value-added chemical recovery from resources.

Rodrigues et al. (2018) discussed about the transition of chemical pulp mills to integrated biorefineries to obtain multiple value-added products from lignocellulosic biomass, instead of just pulp. In their work, they used cellulose, lignin, biofuels, sugars, and specialty chemicals as potential products in the context of a biorefinery. The utilization of Kraft lignin in products like vanillin, syringaldehyde, polyphenols and polymer related materials are examples of the possibility to add value to the pulp-mill side streams.

3. METHODOLOGY

A process based analytical and optimisation method has been used to assess chemical recovery in a typical kraft pulp mill. The analysis was concentrated on the following aspects: black-liquor concentration, operation of the recovery-boiler, clarification of green-liquor, causticization, Lime regeneration, energy recovery and resource utilization. Selected performance indicators were compared between representative baseline and optimised operating conditions.

3.1. Research Design

The methodology was as follows: Identification of process, selection of performance parameters, baseline assessment, optimisation, performance comparison and resource-recovery assessment. The recovery system has been evaluated as an integrated process since changes to one unit may affect the performance of downstream processes.

3.2. Chemical-Recovery System Considered

This system consisted of black liquid evaporation, recovery boiler, smelt dissolving, green liquid clarification, slaking, causticization, white liquid clarification, lime mud washing and lime kiln regeneration. The chemical and calcium recovery cycles were treated as a single cycle to evaluate system performance.

3.3. Performance Indicators

Performance indicators were black-liquor solids concentration, reduction efficiency in the recovery boiler, chemical-recovery efficiency, causticizing efficiency, lime availability, steam generation, specific energy consumption, chemical losses, inorganic-residue generation and process-water requirement.

The following equation was used to determine the main efficiencies:

$$\eta_{CR} = \frac{\text{Recovered reusable inorganic chemicals}}{\text{Total inorganic chemicals entering the recovery system}} \times 100$$

$$RE = \frac{Na_2S}{Na_2S + Na_2SO_4} \times 100$$

$$CE = \frac{\text{NaOH formed}}{\text{Total effective alkali}} \times 100$$

3.4. Process Optimisation

The optimisation scenario was: better evaporation control, stable black-liquor solids, better combustion control of the combustion boiler, reduced losses of green-liquor, optimised lime dosage and causticizing conditions, better lime-mud washing, and stable operation of the lime-kiln. Where technically possible opportunities for process-water and inorganic-residue reuse were also taken into account.

3.5. Data Analysis

Representative baseline and optimised values were compared to assess the changes in chemical recovery, energy generation, chemical losses, and residue generation. Percentage change was calculated as:

$$\% \text{ Change} = \frac{\text{Optimised value} - \text{Baseline value}}{\text{Baseline value}} \times 100$$

The results were analysed at both the unit-level and system-level to ascertain the effectiveness of the proposed optimisation measures.

4. RESULTS AND DISCUSSION

The results are compared to the representative baseline operating conditions and proposed optimised conditions for the Kraft chemical-recovery system. The assessment was concerned with chemical recovery, performance of the recovery boiler, the efficiency of the causticizing and lime cycle, energy utilisation, and resource recovery opportunities. The comparison was used to assess the impact that the individual recovery operation improvements would have on the overall performance of the integrated system.

4.1. Overall Operating Performance

Table 1 shows the representative baseline and optimised values of major operating and performance parameters for the chemical-recovery system.

Table 1: Representative baseline and optimised operating parameters

Parameter	Baseline condition	Optimised condition	Change
Black-liquor solids (%)	68.0	74.0	+6.0 percentage points
Recovery-boiler reduction efficiency (%)	94.2	96.8	+2.6 percentage points

Chemical recovery efficiency (%)	94.8	97.1	+2.3 percentage points
Causticizing efficiency (%)	78.5	83.6	+5.1 percentage points
Lime availability (%)	82.0	88.0	+6.0 percentage points
Steam generation (t/t pulp)	2.05	2.20	+7.3%
Specific auxiliary energy (kWh/t pulp)	58	53	−8.6%
Inorganic residue (kg/t pulp)	19.5	16.8	−13.8%

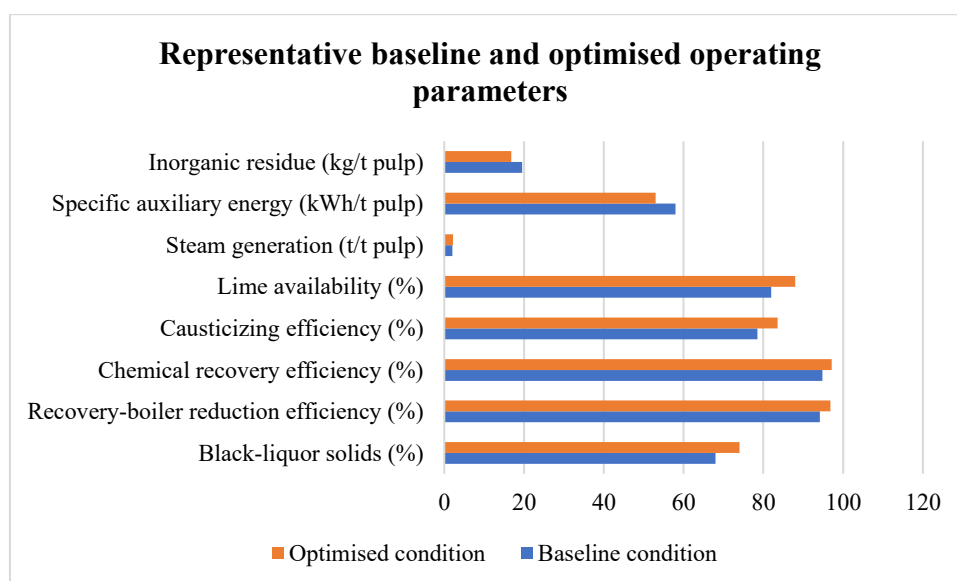


Figure 1: Visual Representation of Representative baseline and optimised operating parameters

The performance of the chemical-recovery system was improved overall in the optimised condition. The number of black-liquor solids rose from 68.0% to 74.0%, which meant that a more concentrated feed could be put into the recovery boiler. The chemical recovery efficiency rose from 94.8% to 97.1%, and the recovery-boiler reduction efficiency by 2.6 percentage points. The improvement in the efficiency of the causticizing section from 78.5% to 83.6% causticizing and 82.0% to 88.0% availability of lime is shown. Furthermore, the steam generation was found to increase by 7.3%, while the specific auxiliary energy consumption and inorganic residue generation were reduced by 8.6% and 13.8%, respectively.

Based on these findings, it is suggested that chemical, energy and material benefits can be achieved at the same time with coordinated optimisation.

4.2. Recovery-Boiler Performance

The recovery boiler plays an important part in the kraft recovery cycle both as a producer of useful thermal energy from the organic part of black liquor and as a recovery system for inorganic chemicals in the form of smelt. The representative recovery-boiler performance, in both the conventional way and the optimised way, is shown in Table 2.

Table 2: Representative recovery-boiler performance

Parameter	Conventional operation	Optimised operation	Improvement
Black-liquor solids (%)	68.0	74.0	+8.8%
Reduction efficiency (%)	94.2	96.8	+2.6 percentage points
Steam generation (t/t pulp)	2.05	2.20	+7.3%
Supplementary fuel requirement (GJ/t pulp)	0.42	0.30	–28.6%
Unburned carbon indicator (%)	1.8	1.1	–38.9%
Chemical loss index	1.00	0.78	–22.0%

The results from the recovery-boiler test showed that optimization of the combustion control and increasing of black-liquor solids improved not only energy recovery but also chemical recovery. The specific steam generation increased by 7.3% with a solids increase of 6.0% from 68.0% to 74.0%. Meanwhile, the supplementary fuel consumption dropped from 0.42 to 0.30 GJ/t pulp, which is a decrease of 28.6%. Further reduction in the unburned-carbon indicator from 1.8% to 1.1% indicated better utilization of the organic fraction of BL. In addition, the chemical loss index fell by 22.0%, reflecting greater recovery of inorganic chemicals that can be recovered during the process. These results show that the recovery boiler is not only an energy generating unit but also a chemical recovery unit. By

optimizing combustion conditions, it is possible to simultaneously optimize two important combustion performance goals.

4.3. Causticizing and Lime-Cycle Performance

The efficiency of chemical regeneration is strongly affected by the performance of the causticizing and the lime-regeneration section. The representative results of such operations are given in Table 3.

Table 3: Representative causticizing and lime-cycle performance

Parameter	Baseline	Optimised	Improvement
Causticizing efficiency (%)	78.5	83.6	+5.1 percentage points
White-liquor active alkali (g/L)	105	112	+6.7%
Lime availability (%)	82.0	88.0	+6.0 percentage points
Lime-mud moisture (%)	32	28	−12.5%
Lime-kiln fuel consumption (GJ/t CaO)	5.8	5.1	−12.1%
Lime-mud loss (kg/t pulp)	13.2	10.9	−17.4%

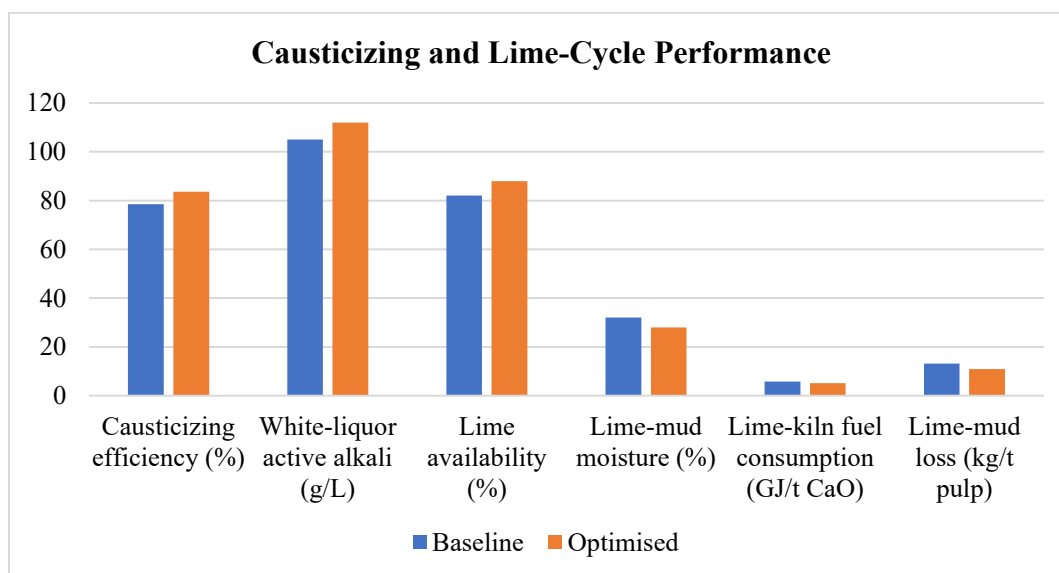


Figure 2: Visual Representation of Causticizing and Lime-Cycle Performance

The optimized condition resulted in an improvement of causticizing efficiency by 5.1 percentage points, from 78.5% to 83.6%. This was coupled with a rise in active alkali in white liquor from 105 to 112g/L

suggesting better regeneration of sodium hydroxide from green liquor. Availability of lime rose from 82% to 88%, indicating better regeneration and utilisation of calcium oxide in the lime cycle.

A decrease in the moisture content of lime-mud from 32% to 28% was also noted. A reduction in moisture content decreased the evaporative thermal load in the lime kiln, and helped to cut lime-kiln fuel consumption 12.1%. Also, the lime-mud loss reduced by 17.4%. The overall changes suggest that the chemical losses can be minimized and operational stability of the white-liquor regeneration can be enhanced with better control of causticizing process, washing the lime-mud and operating the kiln.

4.4. Resource-Recovery Opportunities

In addition to the optimisation of process units, the energy, the chemicals, the water and the inorganic materials can be recovered and reused in the recovery cycle. The summary of the opportunities identified in the analysis is presented in Table 4.

Table 4: Resource-recovery potential within the Kraft chemical-recovery system

Resource	Conventional handling	Optimisation/resource-recovery strategy	Expected benefit
Black-liquor organics	Combustion primarily for energy recovery	Optimised combustion and heat recovery	Increased steam generation and energy efficiency
Na ₂ S and Na ₂ CO ₃	Chemical regeneration through recovery cycle	Improved recovery-boiler and smelt control	Reduced fresh chemical make-up
Lime mud	Reburning with associated process losses	Improved washing, dewatering and kiln control	Reduced lime and sodium losses
Green-liquor dregs	Disposal or limited utilisation	Separation, treatment and potential beneficial use	Reduced solid-waste generation
Process water	Multiple fresh-water inputs	Filtrate and condensate integration	Reduced freshwater requirement
Waste heat	Partial recovery	Heat integration and condensate reuse	Lower thermal energy demand

Based on the resource-recovery assessment, several streams of material and energy from the Kraft recovery cycle can be considered recoverable resources instead of waste streams. The organic portion of black liquor is used as a renewable source of process energy and sodium compounds are recovered and re-used in the pulping process. Better washing and de-watering of the lime-mud can minimize losses of sodium and lime, while enhancing the calcium cycle.

The dregs (green-liquor) from liquidation is another resource recovery opportunity. Appropriate characterisation and treatment of selected inorganic residues may provide opportunities for a beneficial use instead of disposal. Likewise, process condensates and appropriate filtrates can be connected to the mill water circuit to decrease freshwater usage. Another potential opportunity to reduce the total thermal demand for the recovery system is through waste-heat integration.

But, the reuse of residues and internal water recycling should be used with care as it may result in undesirable inorganic elements building up within closed water cycles. Hence, a proper chemical and environmental characterization is needed to determine the suitability of any residue for beneficial uses.

4.5. Overall Performance Analysis

The results reveal the ability of optimisation of the Kraft chemical-recovery cycle to enhance the chemical recovery, energy generation and resource utilisation. The impact of the optimised operating conditions is discussed below.

➤ *Effect of Black-Liquor Solids*

The concentration of black-liquor solids rose from 68% to 74%, which led to an increase of the organic material that can be burned. This helped to increase steam production and decrease supplementary fuels use. Too high solids however can cause liquor to become viscous and have an adverse effect on pumping and atomisation, so an optimum operating range should be ensured.

➤ *Recovery-Boiler Performance*

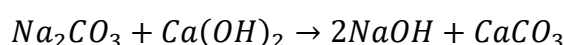
The efficiency of the reduction process in the recovery boiler rose from 94.2% to 96.8%, which indicated the better conversion of the oxidised sulphur into recoverable sulphide. Better combustion also meant that more steam was generated and that there were fewer losses of unburned carbon and chemicals. Therefore, simultaneous energy and chemical recovery requires effective control of combustion air, temperature, oxygen and liquor firing conditions.

➤ *Green-Liquor Management*

The recovery-boiler smelt is dissolved in water to produce green liquor, which consists primarily of sodium carbonate and sodium sulphide, and has suspended dregs. Good clarifications will minimize loss of chemicals and unwanted inorganic material build-up. Better green-liquor management will, therefore, enable a better chemical-recovery efficiency and the better performance of the downstream causticizing.

➤ *Causticizing Efficiency*

The efficiency of the causticizing process rose from 78.5% to 83.6% which means that there is an increase in the conversion of sodium carbonate to sodium hydroxide:



To ensure consistency of white liquor quality and avoid chemical losses, it is important that the dosage of lime, its temperature, mixing, and residence time are maintained at the correct level.

➤ *Lime-Cycle Performance*

The amount of lime available rose from 82% to 88% and the moisture content of lime-mud fell from 32% to 28%. These enhancements have decreased the consumption of fuel in the lime-kilns and decreased the losses of lime-mud. Thus, efficient washing, dewatering and kiln control can maximize recovery of the calcium and help to minimize energy needs.

In general, it is observed that the chemical, energy and material efficiency of Kraft pulp mills could be enhanced via the optimization of the evaporation, the operation of the recovery-boiler, the causticizing, and the lime regeneration in an integrated fashion.

5. CONCLUSION

The study shows that the overall optimisation of the kraft chemical-recovery cycle has the potential to greatly enhance chemical, energy, and material efficiency. The representative optimisation scenario led to an increase in black-liquor solids from 68% to 74%, chemical-recovery efficiency from 94.8% to 97.1%, and reduction efficiency in the recovery-boiler from 94.2% to 96.8%. In addition, there were improvements in the efficiency of causticizing, availability of lime, steam generation, reduction in auxiliary energy consumption, reduction in requirement of supplementary fuels, reduction in chemical losses and reduction in inorganic-residue generation. The results also show that the black liquor, sodium chemicals, lime mud, process water, waste heat and some inorganic residues can potentially be recovered resources. In general, an optimisation process that coordinates the evaporation, operation of the

evaporation boiler, causticization, and regeneration of lime, offers a practical method of enhancing the utilization of the resources, and of promoting the sustainability of Kraft pulp mills.

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