Energy and emission implications of optimized white liquor causticity

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ABSTRACT: Optimizing the causticizing plant offers significant opportunities for energy and emissions savings in kraft mills by minimizing the chemical and water deadload introduced into the recovery cycle via white liquor. Modern control strategies utilize both feedforward and feedback loops to manage causticity, enabling more aggressive targets closer to equilibrium levels.

This paper evaluates the benefits of optimizing white liquor chemistry through a detailed CADSIM Plus simulation model, replicating the chemistry of a Canadian bleached kraft mill that adopted an automated causticizing control system. The control system increased causticity from 77.0% to 82.3% at a fixed total titratable alkali (TTA) of 126.5 grams of sodium dioxide per liter (gNa_2O/L). Modeling this chemistry change indicated a 1.5 metric tons per hour (t/hr) reduction in evaporator steam demand and a 2.8% increase in black liquor higher heating value. Consequently, the improved heating value resulted in a 1.5% rise in recovery boiler steam production and a 5.3% reduction in biomass energy consumption in power boilers, leading to a 4.8% decrease in biogenic carbon dioxide (CO_2) emissions. Additionally, reducing the inorganic and water deadload throughout the recovery cycle may support higher as-fired dry solids targets, enhancing recovery boiler energy efficiency by lowering the water evaporation requirement during black liquor combustion. However, implementing a causticizing control system requires careful assessment of potential lime kiln bottlenecks, as increased causticity demands may affect kiln operations depending on broader mill conditions. Overall, an automated causticizing control system enhances process efficiency, reduces energy consumption and emissions, and positions kraft mills for improved productivity and long-term sustainability.

Application: This study provides kraft mill operators and researchers with quantitative insights into how optimizing white liquor causticity through automated control systems can improve mill-wide energy efficiency, reduce greenhouse gas emissions, and enhance process performance. The findings support further research and industrial adoption of advanced process control to drive sustainability and competitiveness in the pulp and paper sector.

Past studies have identified causticizing plant optimization as a key opportunity for mills to enhance productivity, profitability, and process efficiency by minimizing chemical deadload in the recovery cycle [1,2]. Reducing unnecessary dilution of active alkali chemicals is particularly important, as it can significantly decrease heating and evaporative loads, especially in the black liquor evaporation plant. Two critical parameters influence how causticizing plant operations affect the entire pulp mill: total titratable alkali (TTA) and causticity. This paper builds on previous research by employing advanced modeling to demonstrate how optimizing process chemistry can reduce net energy consumption and overall mill emissions.

Total titratable alkali

In North America, total chemical strength is typically measured as TTA, representing the combined concentration of sodium hydroxide (NaOH), sodium sulfide (Na_2S), and sodium carbonate (Na_2CO_3). Total titratable alkali is expressed in grams of sodium dioxide per liter (gNa_2O/L) or pounds of sodium dioxide per cubic feet ($lbNa_2O/ft^3$), which are common units accounting for mols of sodium in each species [3,4]. The equation for TTA is as follows [5]:

$$TTA = NaOH + Na_2S + Na_2CO_3$$

(typical operating range: 120–130 gNa_2O/L)

The TTA is primarily controlled at the smelt dissolving tank, where weak wash (a dilute solution of green and white liquors), evaporator condensate, or water is used to dissolve the inorganic smelt from the recovery boiler to form raw green liquor. The maximum achievable strength of the final white liquor is determined at this stage, as TTA generally cannot be increased downstream without the addition of concentrated makeup chemicals. Therefore, the TTA at the smelt dissolving tank is a critical control point in determining the final white liquor strength. Excessive weak wash addition to the dissolving tank will result in a lower TTA and will introduce additional water load that must be processed through causticizing, cooking, and evaporation. Conversely, if too little weak wash is added, the resulting increase in TTA can cause pirssonite ($Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$) scaling in the green liquor discharge lines, restricting flow from the dissolving tank to the green liquor clarifier. In addition, elevated TTA levels can slow the causticizing reaction (discussed in the next section) and limit it by equilibrium constraints.

Effective monitoring and control of green liquor TTA are essential for regulating and stabilizing the chemical strength of green liquor as it moves through the liquor cycle. Minimizing TTA fluctuations reduces input variability in the causticizing process [6]. A weak wash dilution system, controlled by a density loop, can further manage green liquor TTA by regulating the weak wash flow to the green liquor before it reaches the slaker. While this trim control system can reduce TTA variability, it will also introduce additional dilution into the process.

Causticity

Causticity measures the proportion of NaOH relative to the combined amount of NaOH and Na_2CO_3, all represented as sodium oxide (Na_2O) and expressed as a percentage [4]. The equation for causticity is as follows [5]:

$$Causticity = \frac{NaOH}{NaOH + Na_2CO_3} \times 100\%$$

(typical operating range: 80%–84%)

Sodium hydroxide is regenerated from Na_2CO_3 through the causticizing reaction, initiated by the presence of calcium hydroxide ($Ca(OH)_2$), provided by lime slaking. The reactions for lime slaking (1) and causticizing (2) are as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2 + Heat \quad (1)$$

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

Causticizing begins in the lime slaker and continues in large mixing tanks (causticizers) that provide residence time for the mass transfer-limited equilibrium reaction to proceed. Causticity is controlled by adjusting the lime dosage to the slaker, typically by regulating the lime mass flow relative to green liquor flow. Higher lime dosages push the reaction closer to its equilibrium causticity limit, increasing causticity. However, excess lime introduced when operating near the equilibrium causticity limit can lead to overliming, which causes several issues, including sliming over white liquor pressure filters, increased solids in white liquor, elevated alkali content in lime mud (leading to lime kiln rings), and scaling in the digester and evaporators due to higher calcium concentrations in the white liquor [7].

Lower causticity targets can prevent over-liming but increase Na_2CO_3 deadload and water carrying the deadload to the liquor cycle. A higher Na_2CO_3 deadload at a fixed TTA reduces active alkali (sodium hydroxide and sodium sulfide) concentration, requiring higher white liquor flow to maintain alkali-to-wood ratios. This increase in liquor flow reduces energy efficiency by increasing heating and evaporative demand, which could lead to process bottlenecks [2]. For instance, increased black liquor volume sent to the evaporation plant raises steam demand to achieve the same percent dry solids (%DS) in the as-fired liquor. In mills with evaporation bottlenecks, this might even reach a point where %DS targets must be lowered, or where production must be curtailed.

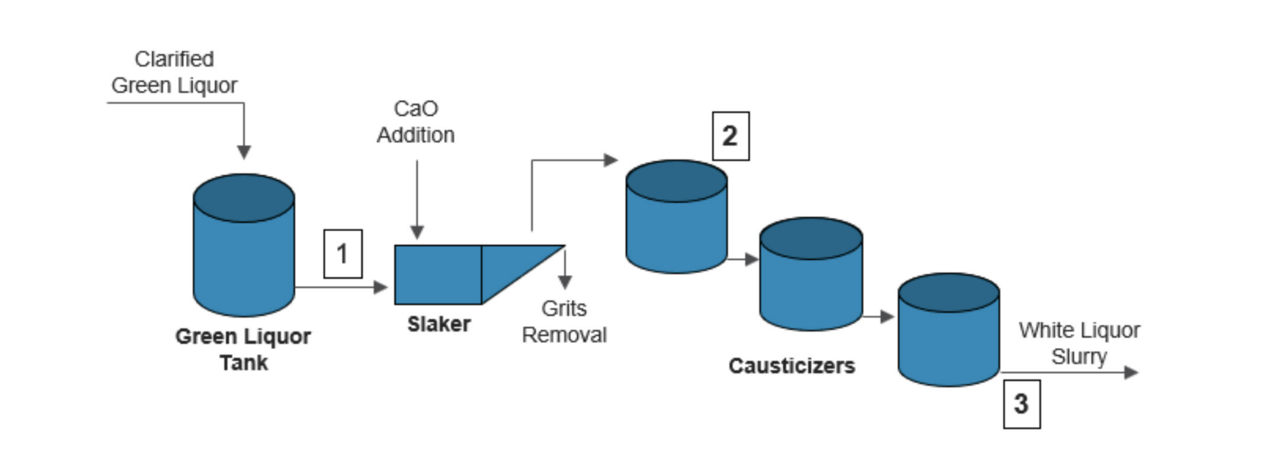
Additionally, increased chemical deadload reduces the heating value of black liquor fired in the recovery boiler, leading to lower boiler thermal efficiency from increased heat losses due to higher smelt flow [2]. A higher Na_2CO_3 deadload also lowers the critical solids of the black liquor (%DS at which scaling from nucleation occurs), impacting where and how aggressively scaling builds up in the evaporator train [8,9].

Modern control strategies employ both feedforward and feedback loops to manage causticity. For example, feedforward control is implemented by analyzing the green liquor quality entering the slaker (Point 1 in **Fig. 1**) and then feedback control is applied at two points within the causticizer train: after the first causticizer (Point 2), where over 90% of the reaction occurs, and after the final causticizer (Point 3), to assess the final white liquor quality. The feedforward and feedback signals are then used to optimize lime dosage from the slaker to set causticity targets near the equilibrium maximum.

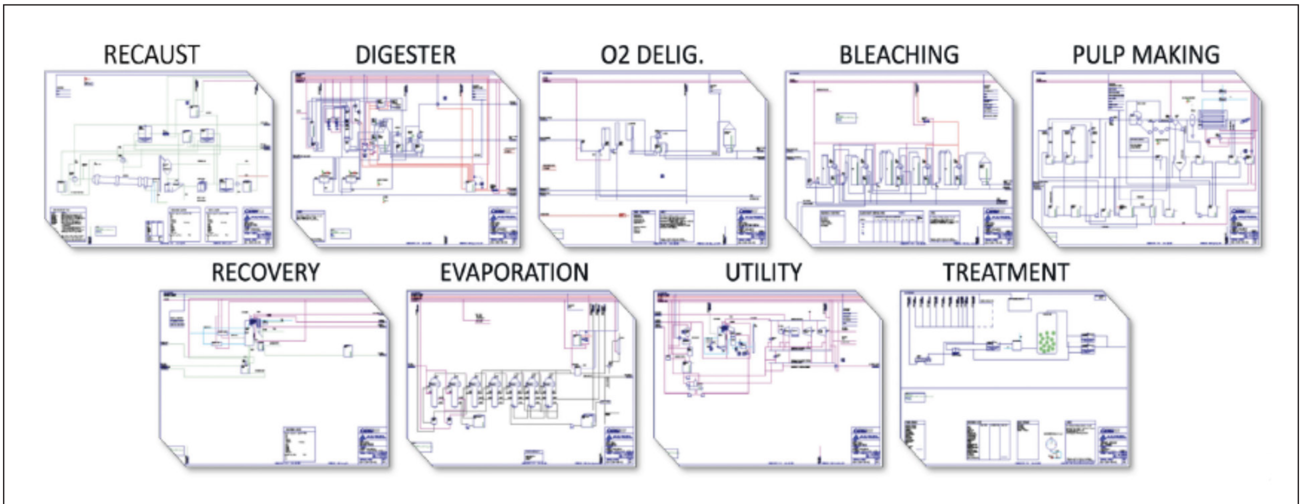
True optimization of total titratable alkali and causticity hinges on frequent and precise monitoring of green and white liquor chemistry. The advent of online liquor analyzers has significantly increased the frequency of these measurements, allowing for better control of process variability. However, accuracy is paramount. Accurate measurements enable the control system to fine-tune causticity targets safely, pushing them closer to the equilibrium limit without over-liming. The more reliable the data, the more confidently and aggressively targets can be set, leading to enhanced process efficiency and optimization that result in decreased mill-wide energy consumption and emissions. This work aims to better quantify the value and payback of investing in these modern control systems.

METHODOLOGY

This paper quantifies the energy and emission implications of optimizing white liquor chemistry using integrated kraft mill modeling that captures cross-departmental interdependencies. The modeling was performed with KraftSIM, a publicly available CADSIM Plus (Aurel Systems; Burnaby, BC Canada) model of a representative Canadian kraft mill with current industry chemistry, efficiency, and technology. This work involved configuring KraftSIM to represent the white liquor chemistry of a Canadian bleached kraft mill before and after implementing an automated causticizing control system in 2013 (model specifications discussed in detail below). Modeling enables a more comprehensive un-



1. Causticizing plant simplified process flow diagram (CaO: calcium oxide).



2. Department sections of the model [10].

derstanding of the mill-wide benefits of improved causticizing control systems, going beyond heuristic interpretation of often volatile and error-prone mill data. By isolating and quantifying the value impact, modeling allows claims to be rigorously evaluated and provides a strong foundation to justify the adoption and investment in modern control systems.

KraftSIM is comprised of nine interconnected departmental drawings, illustrated in **Fig. 2** [10], which enable the characterization of both departmental and cross-departmental impacts of operational or technological changes. This comprehensive approach provides a detailed understanding of the chemistry and energy flows throughout the mill. In addition to CADSIM Plus, other modeling software such as Aspen Plus, WinGEMS, and MATLAB Simulink can also simulate kraft mills, providing diverse mass and energy balance estimates. Process simulation remains vital for understanding the extent of process interactions and quantifying their implications on specific equipment, moving towards supporting industry in better controlling and optimizing their processes. Furthermore, modeling and simulation insights enhance the data-driven decision-making for policy development and accelerate efforts to reduce greenhouse gas emissions, improve sustainability, and secure a competitive future for kraft mills.

The model was configured to produce 931 bone-dry metric tons per day (BDMT/d) of softwood kraft market pulp. Operating conditions, such as chip feed, kappa targets, and dilution factors, were held constant, with changes limited to the white liquor chemistry. The simulated mill consumed 2138 BDMT/d of softwood chips with a pulp yield of 46.5%, employed an effective alkali charge (EAW%) on bone-dry wood of 15.5% and maintained white liquor sulfidity at 27.5% TTA by adding Na_2SO_4 (salt cake) to weak black liquor. The weak black liquor %DS was solved to be approximately 16% DS; the %DS of the as-fired liquor was controlled to 70% DS via low-pressure (LP) steam demand to the evaporators; and the recovery boiler reduction efficiency was set to 93%.

To capture the potential mill-wide impacts of integrating an automated causticity control system, the treated white liquor causticity (post-caustic addition) was increased from 77.0% to 82.3%. This was achieved by increasing the lime feed ratio to green liquor, driving the causticizing reaction closer to its equilibrium limit of approximately 85.0% at a fixed TTA of 126.5 gNa_2O/L. The values of 77.0% and 82.3% represent typical measurements at the case study mill before and after the implementation of a Valmet Inc. automated control system. For context, a causticity of 77.0% is considered low relative to the North American average of 81.5% for mills operating within a similar TTA range.

The automated control system, operational since 2013, has significantly stabilized key white liquor parameters — causticity, effective alkali, and sulfidity — for that mill, leading to enhanced digester performance, including reduced kappa variability and more stable digester operation. By maximizing white liquor strength, the mill has been able to push existing equipment to its limits, debottleneck the liquor cycle through decreased liquor flows in causticizing and recovery departments, and increase production rates. Continuous process optimization efforts have since further pushed TTA to 133.0 g/L and causticity to 82.5%, maximizing productivity and profitability.

RESULTS SUMMARY AND DISCUSSION

The simulation results of before and after integrating the control system (referred to as Mill A and Mill A+), as reflected by changing causticity from 77.0% to 82.3%, are presented sequentially along the liquor flow: treated white liquor, weak black liquor, as-fired liquor, and finally green liquor. This is followed by an analysis of the recovery boiler's performance and the corresponding support from the power boiler. The discussion concludes with the overall emissions and the economic implications for the mill.

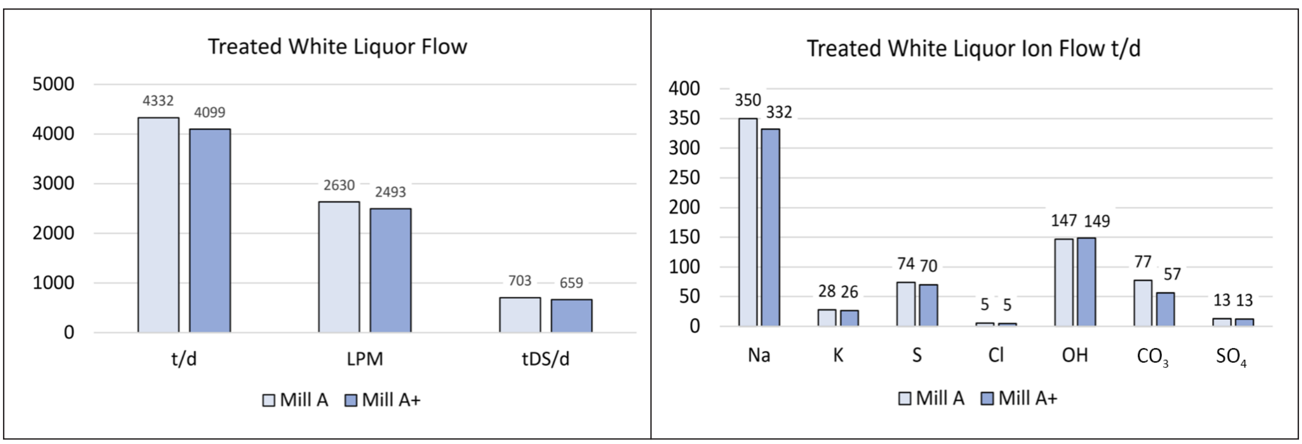
Treated white liquor

The enhanced causticity, attributed to the improved conversion of Na_2CO_3 to NaOH, increases the effective alkali concentration from 88.0 to 92.8 g Na_2O/L. This results in a reduction of 233 metric tons per day (t/d) in the flow of treated white liquor (190 t/d less water), equivalent to 137 liters per minute (LPM). Consequently, there is a decrease of 44 metric tons dry solids/day (tDS/d) in inorganics required to maintain the same EAW% of 15.5%. The properties and flows of treated white liquor for Mill A and Mill A+ are detailed in **Table I** and **Fig. 3**.

Case	[1]Causticity	[2]S(TTA)	[3]EA		[4]AA		[5]TTA	
			gNa_2O/L	tNa_2O/d	gNa_2O/L	tNa_2O/d	gNa_2O/L	tNa_2O/d
Mill A	77.0%	27.5%	88.0	333.2	105.4	399.1	126.5	479.0
Mill A+	82.3%	27.5%	92.8	333.2	110.2	395.7	126.5	454.1

gNa_2O/L: grams sodium oxide per liter; tNa_2O/d: metric tons sodium oxide per day.
[1] Causticity = $NaOH/(NaOH+Na_2CO_3)*100\%$ as Na_2O
[2] Sulfidity (TTA) = $Na_2S / (NaOH + Na_2S + Na_2CO_3)*100\%$ as Na_2O
[3] Effective Alkali (EA) = NaOH + ½*Na_2S as Na_2O
[4] Active Alkali (AA) = NaOH + Na_2S as Na_2O
[5] Total Titratable Alkali (TTA) = NaOH + Na_2S + Na_2CO_3 as Na_2O

I. Treated white liquor properties and flows.



3. Treated white liquor flows before (Mill A) and after (Mill A+) improved causticizing control (t/d: metric tons per day; LPM: liters per minute; tDS/d: total dry solids per day; Na: sodium; K: potassium; S: sulfur; Cl: chlorine; OH: hydroxide; CO_3: carbonate; SO_4: sulfate).

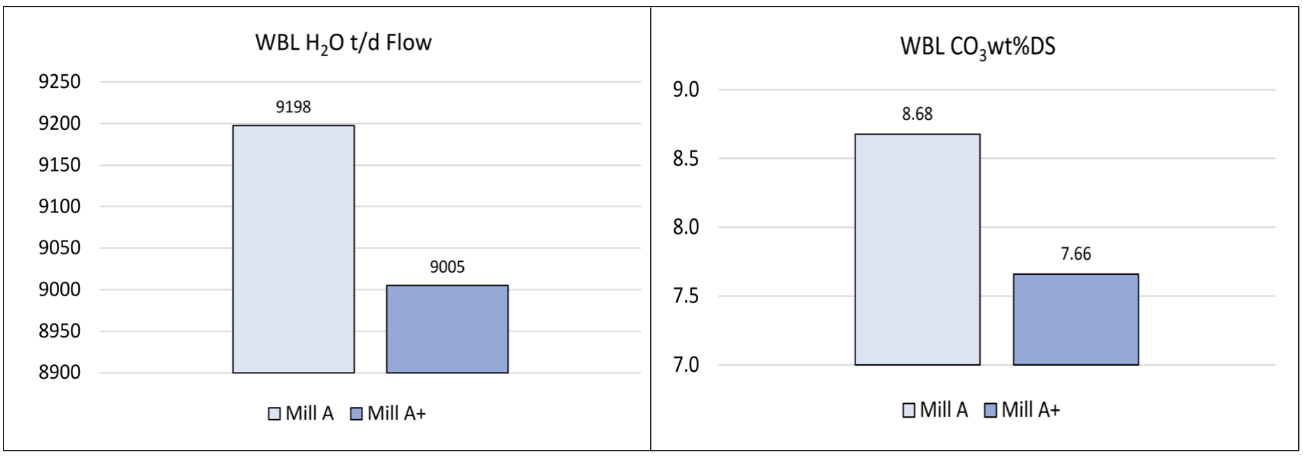
Weak black liquor

The increased causticity delivered several benefits to weak black liquor, as shown in **Fig. 4**. Key outcomes included a 193 t/d reduction in water sent to the evaporation plant and a 1% decrease in carbonate weight percent dry solids (wt%DS), which can help reduce the occurrence of sodium double salt scaling events [8,9,11]. Despite these changes, the %DS of the weak black liquor remained stable at approximately 16%, owing to the reduced Na_2CO_3 deadload, ensuring no significant modifications to evaporation operations were necessary.

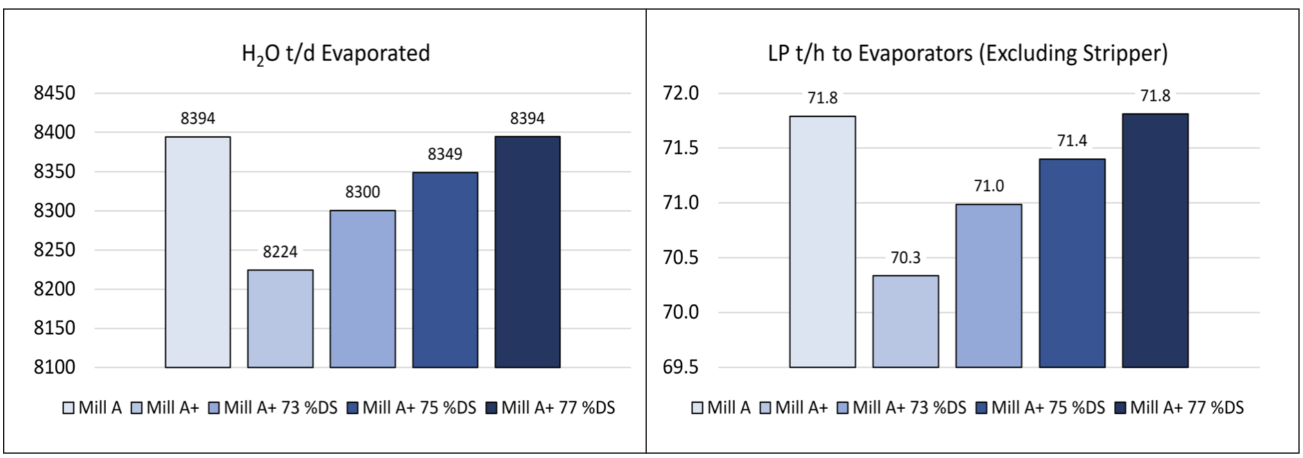
For mills struggling to meet their as-fired %DS targets — or aiming to increase them — the reduced water load and total dry solids being processed by the evaporation plant presents an opportunity to raise as-fired %DS. For example, when the steam supply (heat) to the evaporation plant is operating at its maximum, processing fewer dry solids through the reduction of inorganic dead load, it t/h could enable higher as-fired liquor %DS to be achieved.

To evaluate this potential, an analysis was conducted to model the energy and emissions benefits of increasing as-fired liquor concentrations from 70 %DS to elevated targets of 73%, 75%, and 77 %DS. Implementing an automatic causticity control system to reduce inorganic dead load could allow mills to reach these higher solids levels without increasing maximum steam flow, investing in additional evaporator capacity, or increasing the solids of the weak black liquor by compromising pulp washing or relying on membrane preconcentration technologies. It is also important to note that operating at higher solids levels incrementally increases the %DS through each evaporator body, which may influence which bodies are most susceptible to scaling, depending on the critical solids of the liquor [8,9].

Increasing the %DS of as-fired liquor reduces water content entering the recovery boiler, which mitigates energy losses from water evaporation and decreases flue gas mass flow. However, achieving higher %DS levels may require modifications to recovery boilers, including burner designs, air systems, and firing temperature adjustments, to maintain proper liquor viscosity and droplet size, thereby preventing carryover issues [11]. High-pressure, high-tem-



4. Water (H_2O) and carbonate (CO_3) content of weak black liquor (WBL) before (Mill A) and after (Mill A+) improved causticizing control (t/d: metric tons per day; wt%DS: weight percent dry solids).



5. Water evaporated from weak black liquor and low-pressure (LP) steam to the evaporators before (Mill A) and after (Mill A+) improved causticizing control, including three cases where as-fired liquor %DS is increased without raising maximum steam to the evaporation plant.

perature as-fired liquor storage tanks and circulation systems may also be necessary to maintain flow and avoid excessive scaling [11].

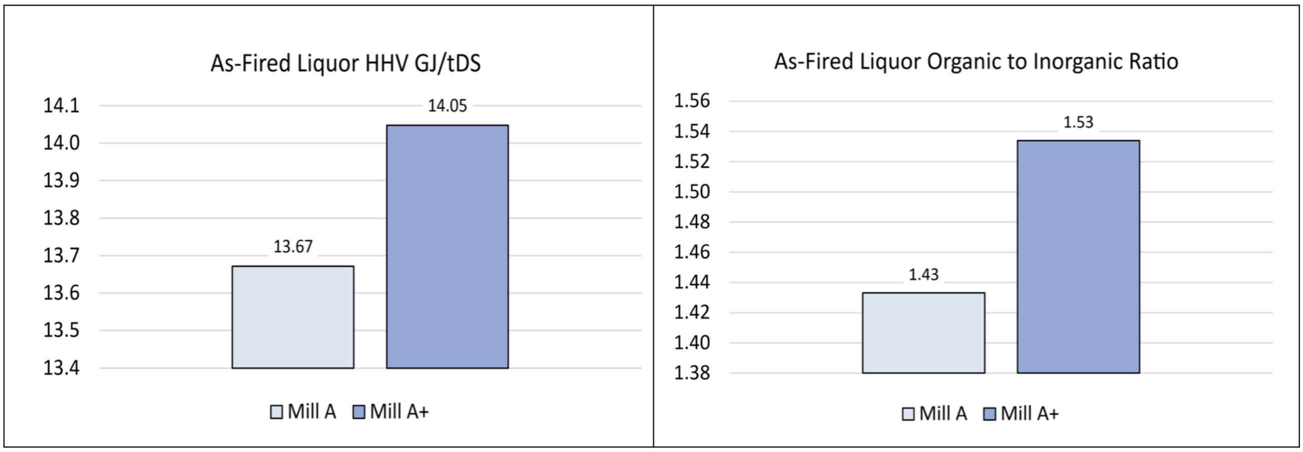
In Mill A+, the increased causticity resulted in 126 t/d less water requiring evaporation and a 1.5 metric tons per hour (t/h) reduction in low-pressure steam (55 psig, 165°C) demand, as shown in **Fig. 5**. These savings were achieved while maintaining the same 70 %DS as-fired liquor, primarily due to reduced white liquor volume to the digester and fewer dry solids processed as a result of the lower Na_2CO_3 deadload. Concentrating the as-fired liquor to 77 %DS was found to require approximately the same amount of steam as Mill A targeting 70 %DS. This indicates that, if the low-pressure (LP) steam supply to the evaporators remains unchanged, the liquor could be concentrated by an additional 7 %DS without additional steam consumption.

As-fired liquor

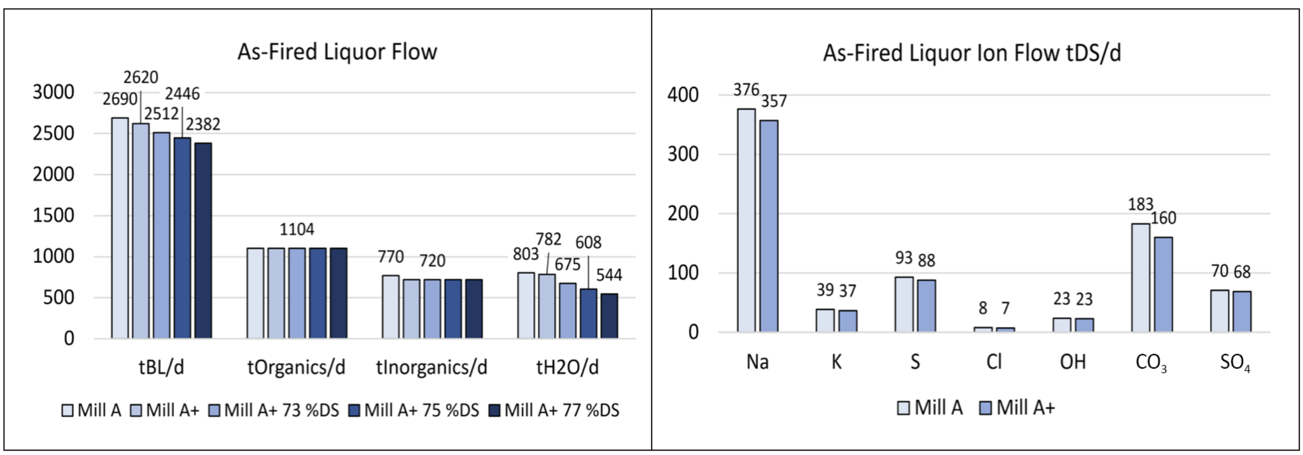
In addition to the steam savings from reduced water sent to the evaporation plant, a causticizing control system can significantly enhance the heating value of black liquor. With the heat provided by the organics burned in the black liquor remaining constant due to steady pulp production and yield in the model, the reduction in inorganics led to a 0.38 gigajoule per metric ton of dry solids (GJ/tDS) (2.8% change) increase in the higher heating value (HHV) of the black liquor and a 0.10 (7.0% change) rise in the organic-to-inorganic ratio, as shown in **Fig. 6**. Mill A+ achieved a reduction of 50 tDS/d in inorganic solids (**Fig. 7**) and 21 t/d less water sent to the recovery boiler (at 70 %DS), with a further reduction of 259 t/d less water in the Mill A+ 77 %DS scenario.

Recovery boiler operation

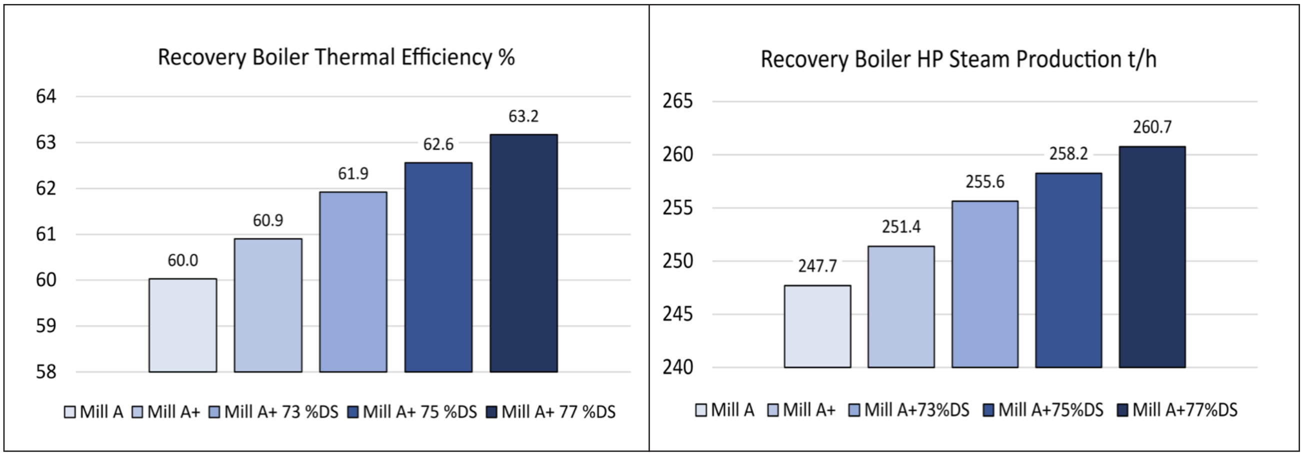
Increasing the heating value and %DS of the as-fired liquor reduces energy losses through the smelt, water evaporation, and flue gases, resulting in improved thermal efficiency (assuming constant excess $\%O_2$ and stack temperature). This efficiency is measured by the thermal energy transferred to boiler feed water (BFW) to produce high-



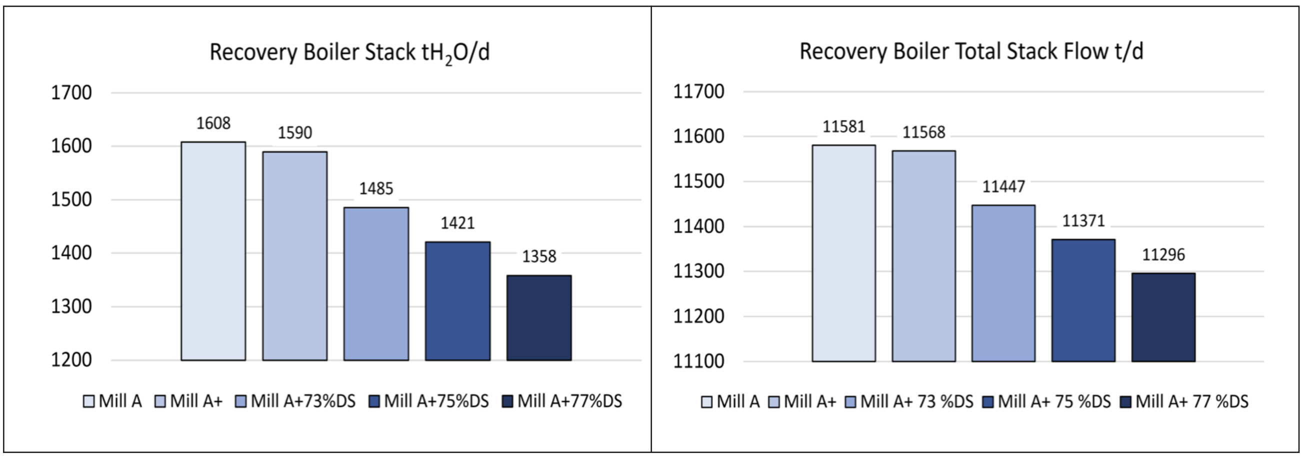
6. As-fired liquor higher heating value (HHV) and organic-to-inorganic ratio before (Mill A) and after (Mill A+) improved causticizing control (GJ/tDS: gigajoules per metric ton dry solids).



7. As-fired liquor flows before (Mill A) and after (Mill A+) improved causticizing control, including three cases where as-fired liquor percent dry solids (%DS) is increased without raising maximum steam to the evaporation plant (Na: sodium; K: potassium; S: sulfur; Cl: chlorine; OH: hydroxide; CO_3: carbonate; SO_4: sulfate).



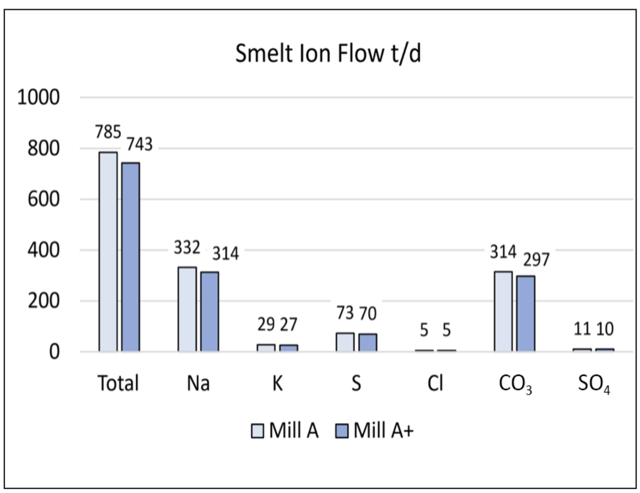
8. Recovery boiler thermal efficiency* and high-pressure (HP) steam production before (Mill A) and after (Mill A+) improved causticizing control, including three cases where as-fired liquor percent dry solids (%DS) is increased without raising maximum steam to the evaporation plant.
**** Recovery Boiler Thermal Efficiency % = $(E_{HPSteam} - E_{Boiler}) / (HHV_{BlackLiquor})$ * 100% where E is thermal energy.***



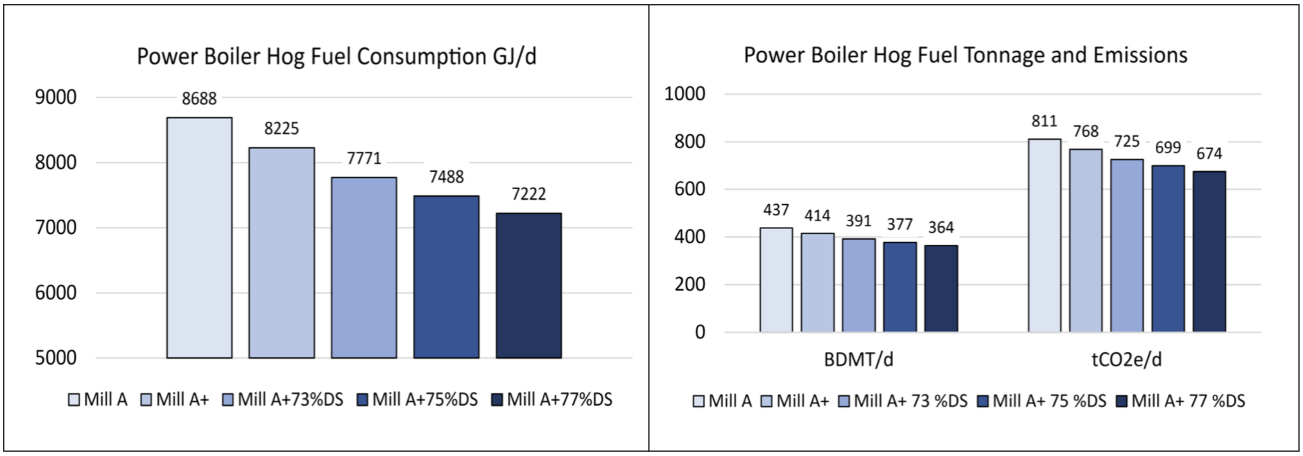
9. Recovery boiler stack flows before (Mill A) and after (Mill A+) improved causticizing control, including three cases where as-fired liquor %DS is increased without raising maximum steam to the evaporation plant (tH_2O/d: metric tons water per day; t/d: metric tons per day).

pressure steam from the combustion energy of black liquor, calculated on an HHV basis. **Figure 8** illustrates that Mill A+ achieves a 0.9% increase in thermal efficiency and produces 3.7 t/h more high-pressure steam (850 psig, 427°C) due to the removal of inorganic dead load. In the Mill A+ 77 %DS scenario, thermal efficiency increases by 3.2%, with an additional 13 t/h of steam production.

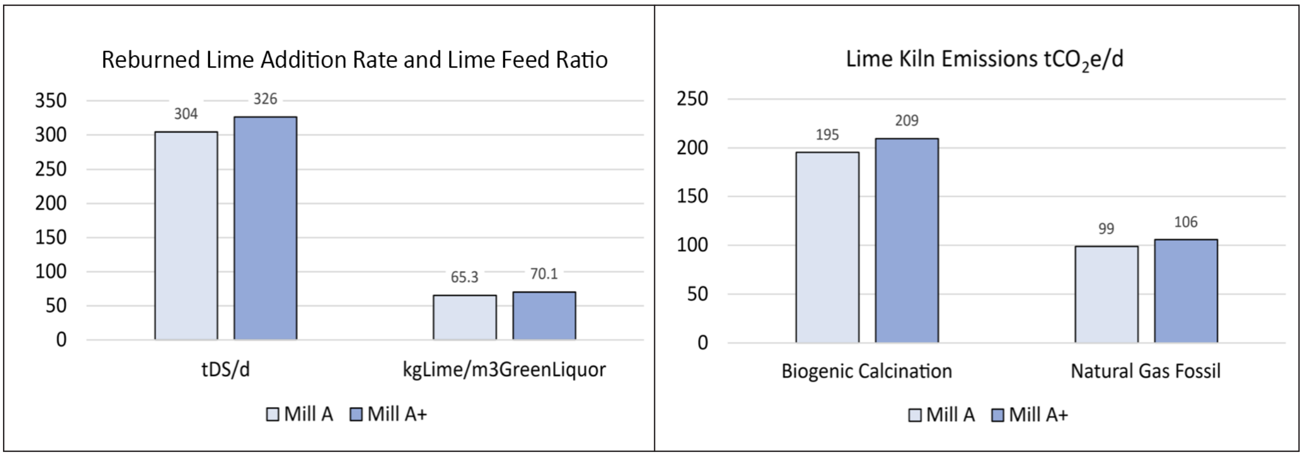
In the Mill A+ case, there is an 18 t/d reduction in water and a 13 t/d reduction in total stack flow, with further reductions of 250 t/d less water and 285 t/d less total stack flow in the Mill A+ 77 %DS scenario, as shown in **Fig. 9**. It is important to note that combustion air (containing 0.5% water by mass) to the recovery boiler is controlled to maintain an oxygen mass% of 3.3% of the total stack flow (including water), which influences the total stack flow in addition to the water in the black liquor. **Figure 10** shows that Mill A+ decreases the total inorganic smelt flow by 42 tDS/d, aligning with the reduction in inorganics carried in by the treated white liquor.



10. Recovery boiler smelt before (Mill A) and after (Mill A+) improved causticizing control (Na: sodium; K: potassium; S: sulfur; Cl: chlorine; OH: hydroxide; CO_3: carbonate; SO_4: sulfate).



11. Power boiler hog fuel firing and emissions before (Mill A) and after (Mill A+) improved causticizing control, including three cases where as-fired liquor percent dry solids (%DS) is increased without raising maximum steam to the evaporation plant (GJ/d: gigagoules/day; BDMT/d: bone-dry metric tons per day).



12. Reburned lime and lime kiln emissions before (Mill A) and after (Mill A+) improved causticizing control (tDS/d: total dry solids per day; tCO_2e/d: metric tons carbon dioxide equivalent per day).

Reducing the mass flow of water to the recovery boiler, which occurs even without increasing %DS, enhances thermal efficiency and reduces the flue gas flow through the boiler. This reduction is crucial for maintaining optimal steam production targets, as recovery boilers often become flue gas flow-limited due to scale buildup that blocks and restricts flue gas flow passages. By lowering the flue gas flow required to maintain steam production, mills can achieve higher production rates between outages, as less flue gas flow is required per metric ton of black liquor solids fired.

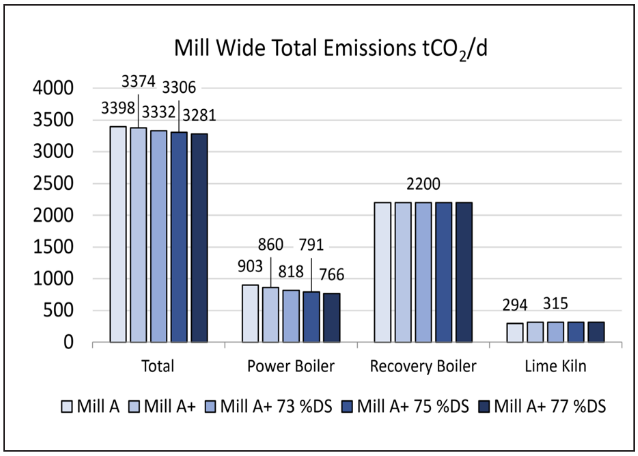
Power boiler operation

The steam balance of the model is managed by adjusting the firing rate of hog fuel (HHV assumed to be 19.86 GJ/tDS) in the power boiler. As inorganic deadload in the as-fired liquor and water entering the recovery boiler is decreased, the steam production of the recovery boiler is improved, resulting in a decreased reliance on hog fuel combustion in the power boiler. **Figure 11** illustrates that in the Mill A+ case, hog fuel consumption is reduced by 463 gigajoules per day (GJ/d) or 23 BDMT/d (5.3% change), resulting in a reduction of biogenic emissions by 43 metric tons carbon dioxide equivalent per day (tCO_2e/d). In the Mill A+ 77 %DS scenario, hog fuel savings increase to 1466 GJ/d or 73 BDMT/d (16.7% change), with biogenic emissions reduced by 137 tCO_2e/d.

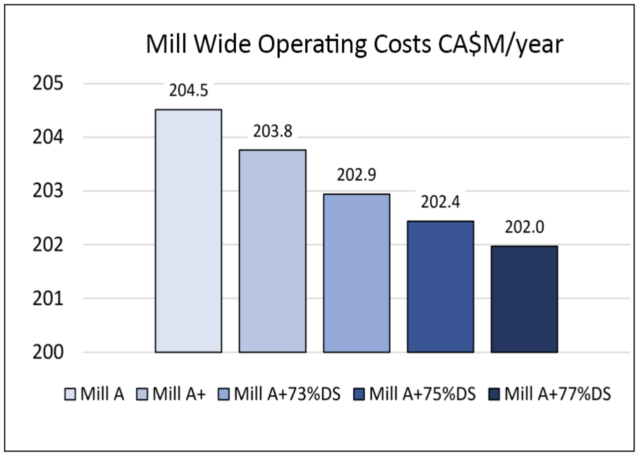
Lime kiln operation

In the model, sulfidity is controlled on a TTA basis, which means that as the conversion of Na_2CO_3 to NaOH is increased, the load on the lime kiln must be increased to provide calcium hydroxide for the causticizing reaction. This increase in sodium hydroxide relative to the amount of sodium sulfide results in more pulping being completed with hydroxide vs. sulfide. In the Mill A+ case, the addition of reburned lime (at 89 wt% CaO) increased by 22 tDS/d (**Fig. 12**), raising the lime feed ratio from 65.3 to 70.1 kg Lime/m³ green liquor. Consequently, natural gas consumption increased by 7%, from 1946 to 2083 GJ/d, leading to an additional 7 tCO_2e/d in fossil emissions, and biogenic calcination emissions increased by 14 tCO_2e/d.

If sulfidity was instead controlled on an active alkali



13. Total emissions before (Mill A) and after (Mill A+) improved causticizing control, including three cases where as-fired liquor percent dry solids (%DS) is increased without raising maximum steam to the evaporation plant (tCO_2/d: metric tons carbon dioxide per day).



14. Annual Operating Costs* (Canadian dollars) before (Mill A) and after (Mill A+) improved causticizing control, including three cases where as-fired liquor percent dry solids (%DS) is increased without raising maximum steam to the evaporation plant.
**** Operating Costs = Cost of Chips + Hogfuel + Natural Gas + Purchased Power + Bleaching Chemicals + Limestone Makeup + Caustic Makeup + Raw Water Influent + Demineralization of Boiler Feed Water + Effluent Treatment + Fossil Emission Taxation. Note that operating costs do not account for labor, maintenance, or asset amortization and depreciation.***

(AA) basis ($NaOH + Na_2S$), the lime kiln load would remain unchanged because the NaOH-to-Na_2S ratio would be kept constant, typically achieved through the addition of more salt cake. Conversely, controlling sulfidity on a TTA basis places a greater reliance on the lime kiln for causticizing and less on sulfur makeup. One drawback of TTA control is that fluctuations in Na_2CO_3 concentration can disrupt the balance between NaOH and Na_2S, causing variability in pulping conditions. These changes can adversely affect lignin removal and delignification rates, leading to inconsistent final pulp quality. In contrast, controlling sulfidity on an AA basis minimizes such variability by maintaining a stable NaOH-to-Na_2S ratio, resulting in more consistent pulping reactions and uniform pulp properties. However, this approach depends more heavily on sulfur makeup chemicals, which can increase operational costs. To provide a conservative estimate, the model was configured to TTA control to represent a mill that was already using all available salt cake. If more salt cake is available for mills, then AA control would step change salt cake addition after increasing white liquor causticity; otherwise, mills could switch to TTA control.

Mill-wide emissions and economics

In the model, the increased causticity resulted in considerable reductions in total emissions (biogenic and fossil) and operating costs. The power boiler continued to fire a fixed amount of 47 BDMT/d (88 tCO_2e/d biogenic emissions) of sludge (assumed to be the same heating value and properties as dry hog fuel), produced from pulp losses in the bleach and pulp machine departments, and a fixed 1 t/d of natural gas (3 tCO_2e/d fossil emissions). Changes in power boiler total emissions are attributed to hog fuel savings.

In the Mill A+ case, hog fuel consumption decreased by 463 GJ/d or 23 BDMT/d (5.3% change), leading to a reduction of biogenic emissions by 43 tCO_2e/d (**Fig. 13**). However, this was offset by an increase in total kiln emissions by 21 tCO_2e/d (14 tCO_2e/d biogenic and 7 tCO_2e/d fossil) due to the increased demand for reburned lime. The recovery boiler emissions remained unchanged as the flow of organics was consistent with fixed pulp production and yield. Overall, Mill A+ resulted in a net decrease of 24 tCO_2e/d in total emissions for the entire mill (sum of power boiler, recovery boiler, and lime kiln), with further reductions of 117 tCO_2e/d in the Mill A+ 77 %DS scenario.

Implementing the Mill A+ scenario led to a reduction in operating costs due to hog fuel savings, amounting to CA$0.7 million annually. In the Mill A+ 77 %DS scenario, these savings increased to as much as CA$2.5 million per year (**Fig. 14**). The cost of biomass was assumed to be CA$100/BDMT.

Overall implications of optimized white liquor chemistry

The implementation of an automated causticizing control system, as represented by a 5.3% increase in causticity in the model, reduced the introduction of inorganics by 44 tDS/d and water by 190 t/d into the recovery cycle from treated white liquor. This reduction in deadload decreased low-pressure steam demand to the evaporators by 1.5 t/h, increased black liquor HHV by 2.8%, and boosted recovery boiler thermal efficiency by 0.9%. Consequently, recovery boiler high-pressure steam production rose by 1.5%, leading to a 5.3% reduction in biomass energy consumption in the power boiler. However, with the sulfidity held constant on a TTA basis, lime production in the kiln increased by 7.2%, as more of the pulping is accomplished with sodium

Case	Causticity	Recovery Boiler			Power Boiler		Lime Kiln		Total Mill	
		BL HHV, GJ/tDS	Thermal Efficiency, %	HP Steam, t/h	Hog Fuel, GJ/d	Total tCO_2e/d	Lime tDS/d	Total tCO_2e/d	Total tCO_2e/d	Costs, $M/y
Mill A	77.0%	13.67	60.0%	247.7	8688	903	304	294	3398	204.5
Mill A+	82.3% (5.3%)	14.05 (2.8%)	60.9% (0.9%)	251.4 (1.5%)	8225 (-5.3%)	860 (-4.8%)	326 (7.2%)	315 (7.1%)	3374 (-0.7%)	203.8 (-0.3%)
Mill A+ 77 %DS	82.3% (5.3%)	14.05 (2.8%)	63.2% (3.2%)	260.7 (5.2%)	7222 (-16.9%)	766 (-15.2%)	326 (7.2%)	315 (7.1%)	3281 (-3.4%)	202.0 (-1.2%)

BL HHV: black liquor higher heating value; GJ/tDS: gigajoules per metric ton dry solids; HP: high pressure; t/h: metric tons per hour; GJ/day: gigajoules/day; tCO_2e/d: metric tons carbon dioxide equivalent per day; tDS/d: metric tons dry solids per day.

II. Summary of case results.

hydroxide. The increased load on the kiln resulted in a 7.1% rise in total (fossil and biogenic) kiln emissions. Overall, the automated control system decreased total mill emissions by 0.7% and decreased operating costs by 0.3%. The key outcomes and changes from the Mill A, Mill A+, and Mill A+ 77 %DS cases are summarized in **Table II**.

By leveraging the additional evaporator capacity gained from reduced inorganic and water deadload, the Mill A+ 77 %DS case, representing a mill where it is possible to increase the as-fired solids target, further amplified savings. Targeting a 77% as-fired %DS, recovery boiler thermal efficiency improved by 3.2%, high-pressure steam production increased by 5.2%, and biomass energy savings reached as high as 16.9%. This scenario led to a 3.4% reduction in total mill emissions and decreased operating costs by 1.2%.

If the model were configured for sulfidity control on an AA basis instead, NaOH-to-Na_2S ratio would remain constant, resulting in no changes to kiln loading or fossil fuel emissions. However, controlling sulfidity on a TTA basis, as used in this model, provides a more conservative estimate of the potential increase in kiln operation required to achieve higher causticity targets.

Impact on evaporation and causticizing plants

Maximizing white liquor causticity and effective alkali levels reduces the water deadload circulating within the liquor cycle, effectively debottlenecking both the evaporation and causticizing plants. In the evaporation plant, this reduced water load offers several benefits: increased liquor solids throughput to support higher mill production, greater dilution in the washroom to improve soda recovery, or increased as-fired liquor solids targets for the same maximum steam flow, as demonstrated in this study's modeling efforts.

Similarly, the causticizing plant benefits from reduced green liquor volumetric flow, achieved by minimizing weak wash addition. This increases residence time in the slaker and causticizers, allowing for more complete slaking and causticizing reactions. For example, a 5% increase in liquor strength corresponds directly to a 5% debottlenecking of the causticizing process, enhancing overall efficiency and throughput.

Stabilizing white liquor quality and digester operation

While maximizing white liquor strength does not directly enhance digester performance, stabilizing white liquor quality has significant downstream effects that were not necessarily captured by the modeling effort in this work. Consistent white liquor composition promotes stable cooking conditions, which can improve pulp yield, reduce bleaching requirements, and — most critically — deliver stable pulp quality for paper machine production, enhancing end-product consistency. Beyond the modeled energy and emissions savings from the automated control system, the real mill implementation of the case study system demonstrated several benefits. Stabilization of causticity, effective alkali, and sulfidity levels resulted in more consistent pulping, with reduced variability in kappa number (an indicator of residual lignin content). Furthermore, the reduction in inorganic and water deadload debottlenecked the causticizing, evaporation, and recovery departments, enabling increased production rates.

Minimizing sodium carbonate deadload and improving recovery boiler efficiency

Reducing Na_2CO_3 deadload lowers the carbonate wt%DS in weak black liquor, mitigating scaling in evaporators. Additionally, the reduced water load entering the recovery boiler decreases flue gas flow per metric ton of black liquor solids fired, relieving pressure on critical flue gas systems, including the induced draft fan and precipitator. Reduced flue gas flow can also help lower the flue gas temperature at each boiler stage, allowing operators to manage ash deposition within the superheater where scaling is more easily controlled, rather than in the generating bank.

Integrated considerations for implementation

The maximum achievable savings from implementing a causticizing control system depend on mill-specific factors and constraints. A thorough evaluation should include: the design capacity of the lime kiln and causticizing plant; condition and adequacy of existing controls, such as green liquor temperature regulation and lime addition systems; and the potential emergence of new bottlenecks as production and efficiency are maximized. Tailoring the system to the mill's unique conditions ensures that process and equipment constraints are addressed to ensure the full potential of optimized causticizing control is realized.

CONCLUSION

The implementation of an automated causticizing control system offers transformative benefits for kraft mill performance, as demonstrated by the comprehensive modeling and analysis in this study. By optimizing lime dosage to achieve white liquor causticity levels closer to equilibrium, the system reduces chemical and water deadloads within the recovery cycle with minimal risk of over-liming. This optimization extends benefits beyond the causticizing plant, resulting in decreased steam demand, fewer scaling events, and increased black liquor HHV. The improved HHV then leads to improved thermal efficiency and steam production in the recovery boiler, and reduced reliance on power boiler support. These improvements collectively translate to significant energy and emissions savings, along with increased profitability.

Further gains can be realized from the reduction of solids processed by the evaporation plant, allowing for higher solids levels at the same maximum steam flow, thereby improving energy efficiency and reducing emissions. While the control system provides a host of advantages, potential trade-offs include higher lime kiln emissions if a mill controls sulfidity on a TTA basis and cannot transition to an

ABOUT THE AUTHORS

We studied this topic because the research aligns with the mandate of our organization, which is dedicated to industrial systems optimization, decarbonization, and energy and resource utilization efficiency. This research builds on the value of integrated process modeling, particularly using KraftSIM to investigate the benefits of optimized white liquor causticity.

The most challenging aspect of this research was redesigning and tuning the chemistry control loops in KraftSIM from a liquor storage control perspective to one that allows for both TTA and causticity to be set. Modification of the control schemes came from team discussions and collaboration with modeling experts.

Through this study, we discovered how much tangible energy and emissions benefits can come solely from integrating an automatic analyzer that helps operators better control and optimize white liquor causticity. The most surprising finding was that the actual mill that invested in the analyzer continues to push the causticity and total titratable alkali (TTA) of their white liquor to the limit in order to benefit the entire recovery cycle.

Mills can quantify potential savings from the information contained in this research, as well as use KraftSIM to investigate their mill context. Mills could then contact vendors to work toward integration of control systems in the recausticizing plant.

Our next step may be to further investigate the modification of white liquor causticity in combination with TTA changes, along with changing the sulfidity control from a TTA to an active alkali (AA) basis. This would be an insightful sensitivity analysis to undertake.

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AA control basis due to limited sulfur makeup capabilities. Despite these challenges, the overall net effect remains positive, with reductions in both biogenic and fossil emissions, along with economic gains from reduced biomass consumption, not to mention possible downstream effects such as more stable product quality and opening the path to further debottlenecking.

This study highlights the critical role of integrated mill modeling in optimizing the kraft recovery cycle. Accurate process measurements are essential to enable control systems to fine-tune causticity targets, pushing them closer to the equilibrium limit without risking over-liming. Ultimately, an automated causticizing control system enhances process efficiency, reduces energy consumption and emissions, and positions mills for greater productivity and sustainability, making it a valuable tool for staying competitive in an increasingly resource-conscious industry. **TJ**

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