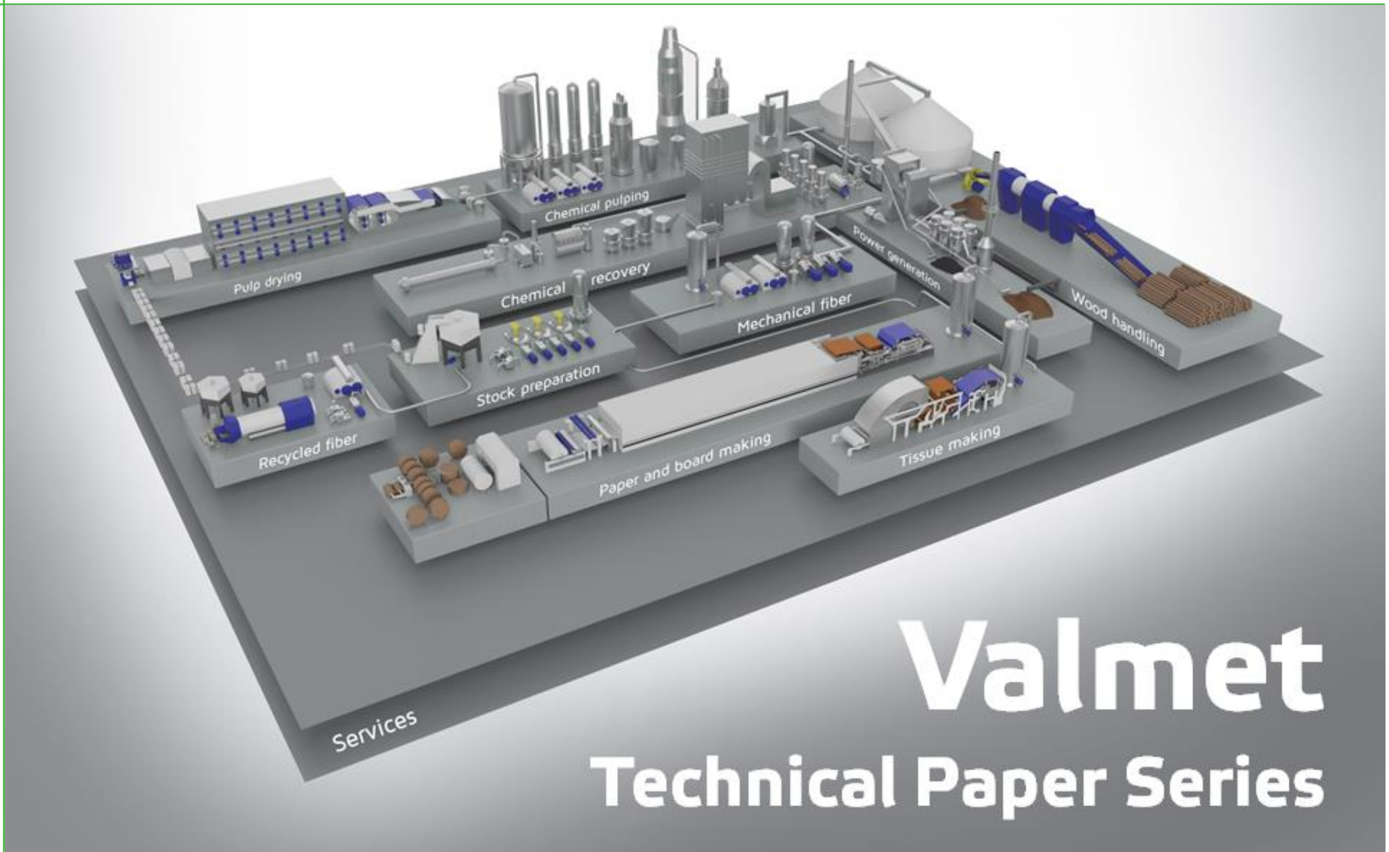


# Reduction Rate Control


## Executive Summary

A recovery boiler's main control variables of reduction rate were studied and the performance of the Valmet Recovery Analyzer's online reduction rate measurement was evaluated in real recovery boiler conditions. The main objectives were to examine which control variable had the most significant effect on reduction rate and to find out how well the analyzer worked under changing burning conditions.

A set of step change adjustments were performed on a recovery boiler's main control variables in order to create desired changes in burning conditions. Evaluation of the analyzer performance was done by comparing measured reduction rate response to expected theoretical behavior, i.e. the reduction rate actual response to performed changes versus the reduction rate expected response according to theoretical knowledge.

The analyses of performed tests indicated that the reduction rate measurement provided reasonable and reliable results under changing burning conditions. Because of the complex nature of recovery boiler process and char bed chemistry, there are several process variables which affect reduction rate but cannot be manipulated, let alone kept constant.

## Introduction

Kraft pulping is based on delignifying wood by a solution consisting mainly of sodium hydroxide (NaOH) and sodium sulfide ($Na_2S$). The solution is generally known as white liquor, and after being used in pulping it can be regenerated in the chemical recovery cycle. In the causticizing process sodium carbonate ($Na_2CO_3$) in green liquor is converted into sodium hydroxide, while sodium sulfide is regenerated as a result of black liquor burning in the recovery boiler. A high reduction rate is preferable because sodium sulfate cannot be treated later and it does not take part in causticizing reactions, which makes it an unfavorable dead load chemical. Sodium sulfide does not take part in causticizing reactions either.

Performance of the chemical recovery process has a major influence on the overall effectiveness of Kraft pulping, as the quality and amount of fresh cooking chemicals regenerated have a direct effect on liquor consumption at the digester and on the amount of make-up chemicals needed to maintain sufficient sodium content in the chemical cycle. The dead load in the process is also largely determined by the conversion efficiencies.

In general, the reduction rate of sodium sulfate in recovery boiler smelt depends on the amount of carbon in the char bed and the lower furnace temperature. Reduction is help by the presence of carbon, and hindered by the presence of oxygen. Furthermore, higher temperatures in the lower furnace increase the rate of reduction, whereas lower temperatures decrease it.

Reduction reactions by char:

$Na_2SO_4 + 2\ C \rightarrow Na_2S + 2\ CO_2$

$Na_2SO_4 + 4\ C \rightarrow Na_2S + 4\ CO$

A rate equation by Grace et al. (1988) for the reduction of sulfate by char (according to Vakkilainen, 2004) is:

$$\frac{\partial [SO_4]}{\partial t} = -K_{Red} \frac{[SO_4]}{B + [SO_4]} C\, e^{\frac{E_a}{RT}} \qquad 5\text{-}15$$

The constants measured for Kraft char were

| | | |
|---|---|---|
| $K_{Red}$ | = | $1.31 \pm 0.41 * 10^3$, 1/s |
| B | = | $0.022 \pm 0.008$, kmol/m$^3$ |
| $E_a$ | = | 122, kJ/kmol |

(Note: C should be [C], meaning the concentration of carbon in melt [kmol/m$^3$]).

According to equilibrium calculations (Hupa 2008), the reduction of sulfate in proceed to 100%, but in practice, chemical kinetics limit the reaction rate and prevent this.

Carbon content of the smelt and smelt fluidity set the limits for a practical maximum reduction rate. The maximum reduction rate when analyzing from the smelt is ~96-97% and therefore when analyzing from the green liquor it is between 94-95%. Higher operation points will be typically seen as a high carbon concentration in green liquor clarification or, for example, in lime circulation.

In addition to carbon, also carbon monoxide, hydrogen, and water can reduce sodium sulfate. However, Hupa (2008) cites Adams and Frederick (1988) by saying that the reduction by char carbon is about two orders of magnitude faster than with these gases.

Precise reduction rate control has been an extremely challenging task to achieve by manual operation. Liquor characteristics and therefore combustion conditions are constantly changing, and arranging frequent enough feedback from the reduction rate is very labor intensive and increases safety risks of field operations.

Reduction rate can be managed when combustion controls are arranged so that primary external disturbances such as boiler load, liquor dry solids or, for example, liquor heat value have minimum impact to char bed conditions and stability.

When combustion controls can master the char bed conditions, reduction rate can be manipulated by controlling temperature and oxidization conditions at the char bed combustion area.

## Online recovery liquor analyzer

The Valmet Recovery Analyzer (Alkali-R) is the third-generation Valmet process titrator (Kokkonen 2014) specially developed for online monitoring and closed loop control of the recovery boiler and causticizing process. The analyzer is a fully automatic, online sampling and titration analyzer for green liquor, causticizing and white liquor. Using a field-proven online sampling system and autotitrator, it provides outputs for control, based on standard process chemistry titration results.


The analyzer system consists of a sample unit, with up to 16 sample points, and a measurement unit with one or two titration modules. With one titration module, the analyzer performs a titration every 7–8 minutes, and a second titration module can halve the analyzing time to 3–4 minutes.

In a typical dissolving tank application, samples are extracted from dissolving tank A and B lines, or just before the stabilization tank. Before analyzing, samples are processed in the sample processing module and dregs are separated from the sample by sedimentation. Then the sample is pumped into a sample coil, from which a multifunctional burette dispenses it into the titration cup.

The analysis is based on the ABC-titration procedure (Standard SCAN 30:85), the most common method in kraft pulp mill laboratories. The analyzer measures the absolute values of sodium hydroxide (NaOH), sodium sulfide ($Na_2S$) and sodium carbonate ($Na_2CO_3$) and reports effective alkali (EA), active alkali (AA), total titratable alkali (TTA), causticizing degree (CE%) and sulfidity (S%). The additional sodium sulfate ($Na_2SO_4$) titration with barium chloride enables the determination of reduction rate.

The benefits of utilizing a liquor analyzer vs. the traditional mill laboratory are clear. The analyzer provides absolute values of liquor chemistry at very high frequency, without human errors in sample collection or analysis work. The liquor analyzer also eliminates safety risks, since exposed handling of liquor or analysis chemicals are unnecessary.

## Recovery boiler combustion control principle

Recovery boiler combustion optimization can be dived to two main control functions, feedforward controls and feedback controls. Feedforward controls (**Figure 1**), take care of char bed stabilization and execute basic tasks of the best practice combustion controls. Firing rate, liquor dry solids and liquor specie are examples of feedforward variables.

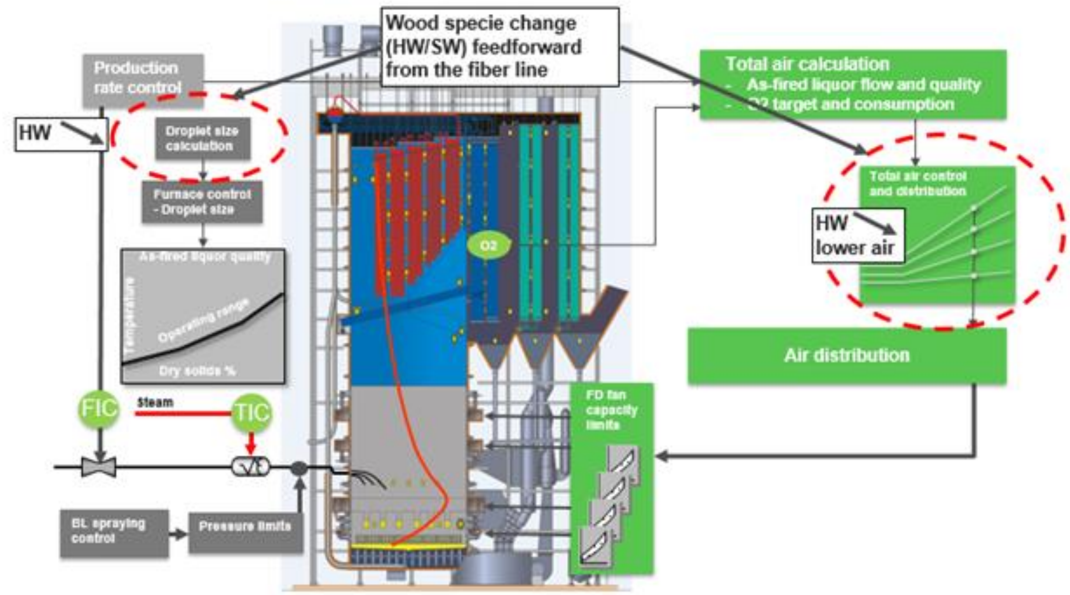


*Figure 1. Recovery boiler optimization, feedforward controls*

Feedback functions (**Figure 2**) execute various corrections to process control parameters, for example air volume, air distribution and liquor temperature, in order to keep reduction rate at the desired target.

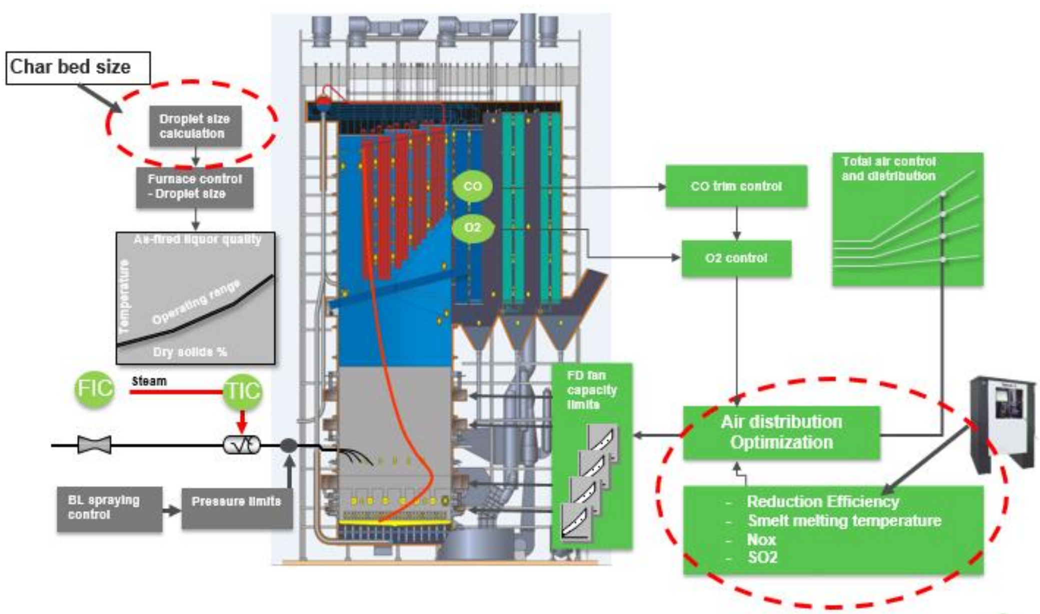


*Figure 2. Recovery boiler optimization, feedback controls*

Feedback controls will also take care of emission management (NOx, CO, $SO_2$) and make sure the char bed temperature is high enough in order to ensure steady and safe smelt flow to dissolving tank.

## Pilot tests at Stora Enso Kemi

### Test mill and recovery boiler

Controls were realized at the Stora Enso Veitsiluoto mill in Kemi, Finland, which has one continuous digester cooking both, soft and hard wood. Species are switched from hard to soft wood and back normally every 24-36 hours. Burning liquor quality changes constantly at the recovery boiler and causes challenges for stable burning.

The Veitsiluoto recovery boiler has been in production several decades. The boiler has been upgraded and modified several times by two major boiler constructors during its history. Modifications includes flue gas channel, superheater, economizer and furnace modifications along with combustion air and liquor nozzle changes. Currently, the boiler is a one-drum boiler with three combustion air levels: primary, secondary and tertiary. Burning liquor is sprayed from all four walls above the secondary air level using spoon type nozzles.

The boiler's process is controlled by Valmet automation's DNA DCS including Valmet Recovery Boiler Sootblowing and Burning Optimizers. Optimization controls have been constantly used for 20 years.

### Start-up and tuning

Before start-up optimization, application and running models were tuned to handle burning liquor quality changes as stably as possible. Also, running models were tuned such that process stability state was similar with all burning liquor qualities. In addition, maintenance for the Alkali-R analyzer was carried out. After stabilization of process reduction efficiency controls were implemented into optimization controls.

Reduction efficiency controls were started up using control principles and parameters that were specified based on the data analysis and testing. During tuning, process data related to controls functionality were gathered and necessary parameters were modified to reach and stabilize the target.

After each set of parameter modifications, there were at least two to three days of monitoring time to gather and analyze results from burning with all liquor qualities. Again, based on process analysis, new controls parameters were specified. This iteration loop was repeated several times.

Reduction control tuning took about three weeks in order to reach a control accuracy level satisfactory for actual testing.

### Reduction control testing

Before testing started, a last modification was carried out for control parameters. More room was given for control actions. Testing was carried out by making target changes to different directions in 1% or 2% steps. Testing lasted approximately two months.

## Results

**Figure 3** shows tuning and test run periods in one trend. The red background indicates a time period without reduction efficiency control. The yellow background is the tuning phase and the green background shows the test phase. Reduction Rate Average without reduction rate control was 93.6% (STDev 1.96). Reduction Rate Average with reduction rate control was 95.3% (STDev: 0.67).

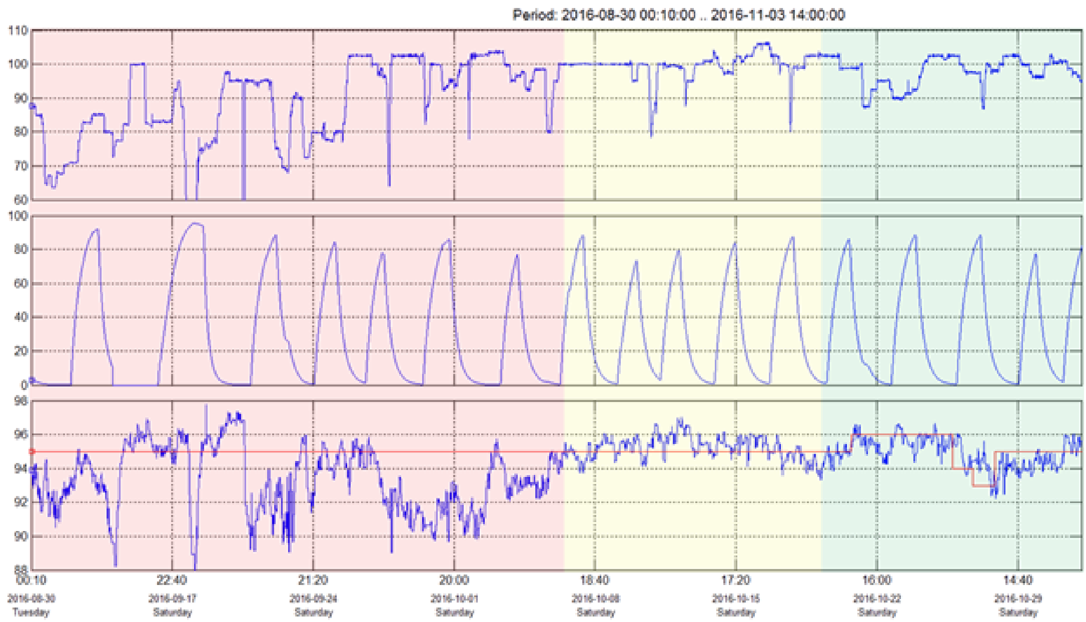


***Figure 3. Top trend area: Boiler Load, middle trend area: softwood percentage, bottom trend area: reduction efficiency (red signal: target and blue signal: measurement).***

**Figure 4** shows test run results. Target changes were relatively small (1% or 2%) because in a live running mill efficiency should be kept high at all times. Despite small target steps, reduction measurement follows target changes within a reasonable time delay. Notice that boiler load and liquor quality changes are causing a minor effect to reduction.

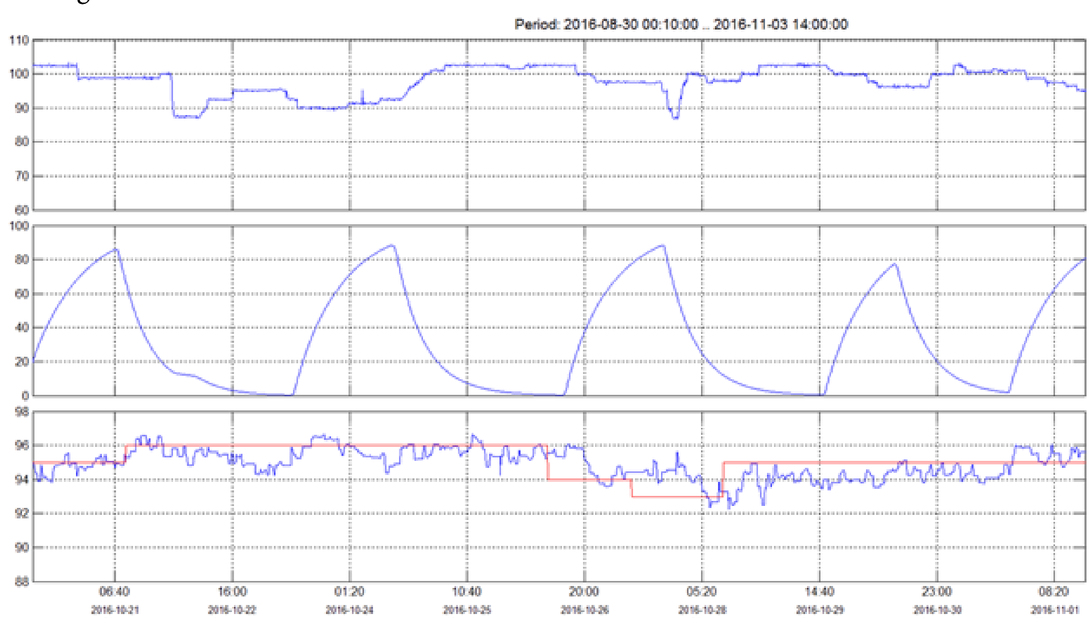


***Figure 4. Test run period. Top trend area: Boiler Load, middle trend area: softwood percentage, bottom trend area: reduction efficiency (red signal: target and blue signal: measurement).***

## Operational costs related to reduction rate

A higher reduction rate means that less dead load (ie. $Na_2SO_4$) and also associated water is circulating in the recovery cycle. Due to higher $Na_2S$ concentration TTA is higher and white liquor is stronger which mean that less white liquor is needed in the cooking process. Typically, water to wood ratio is kept constant during cooking which is accomplished by circulation black liquor replacing the decrease in white liquor. Therefore, the energy savings in the cooking process is relatively small, but the potential is larger in the evaporation plant.

When less water needs to be evaporated, extraction steam consumption can be decreased. But it is also possible to increase the black liquor dry solids content when consuming the same amount of extraction steam. This yields to more steam generation in the recovery boiler and is more beneficial from an electricity point of view.

Causticizing benefits from the higher TTA as a lower water amount leads to longer retention times. In some cases, where causticizing is the bottleneck, it is possible to increase pulp production quite dramatically.

Evaporation capacity is not possible to increase as much, because the washing water amount in evaporation is not directly affected by $Na_2SO_4$ concentration. However, lower $Na_2SO_4$ concentration increases the critical dry solids content (i.e. the dry solids concentration where particles causing fouling start to form) meaning that the washing sequence doesn't need to be as frequent. This has not been included in the following calculations.

Also, the recovery boiler is influenced over time by higher reduction. Even though the heat required for reduction rate increases, steam generation in the recovery boiler increases due to following reasons:

- Black liquor heating value is higher due to less inorganics in the black liquor.
- Smelt heat losses decrease due to less inorganics in the black liquor.
- Water amount to be evaporated is decreased as black liquor contains less water associated to dead load.

Additionally, the flue gas amount decreases since less water is evaporated, which makes pulp production increase possible if flue gas ID. fans or electrostatic precipitators (ESP) are the bottleneck. It is important to note that if the recovery boiler is limited from the steam side, pulp production must be lowered.

Since effective alkali on wood is typically kept constant, if more $Na_2S$ is available, less NaOH is needed for the same cooking charge. Consequently, the lime kiln doesn't need to produce as much CaO for the causticizing reaction which means oil/gas savings or more capacity in the lime kiln.

To illustrate the economic potential for reduction rate control, an example case is presented in **Figure 5 (next page)**. The imaginary case is a 2000 Adt/d (700 000 Adt/a) softwood pulp mill with a bleaching plant and oxygen delignification. Reduction rate is increased from 90% to 95% whereas TTA and causticizing efficiency (CE) are kept constant at the levels of 160 g NaOH/l and 81%. Grey columns show the increase in electricity production in kilowatts with a total increase of roughly 1MW. Additionally, 670t less oil is needed in the lime kiln annually. Green columns indicate how much pulping capacity can be increased if one of the departments is a bottleneck. Debottlenecking evaporation yields an increase of 10 Adt/d (+0.5%) and debottlenecking causticizing/lime kiln gives 34 Adt/d (+1.7%).

The condensing turbine plays a big role in electricity production calculations, because without it low pressure (LP) steam savings (especially in the evaporation plant) wouldn't generate more electricity.

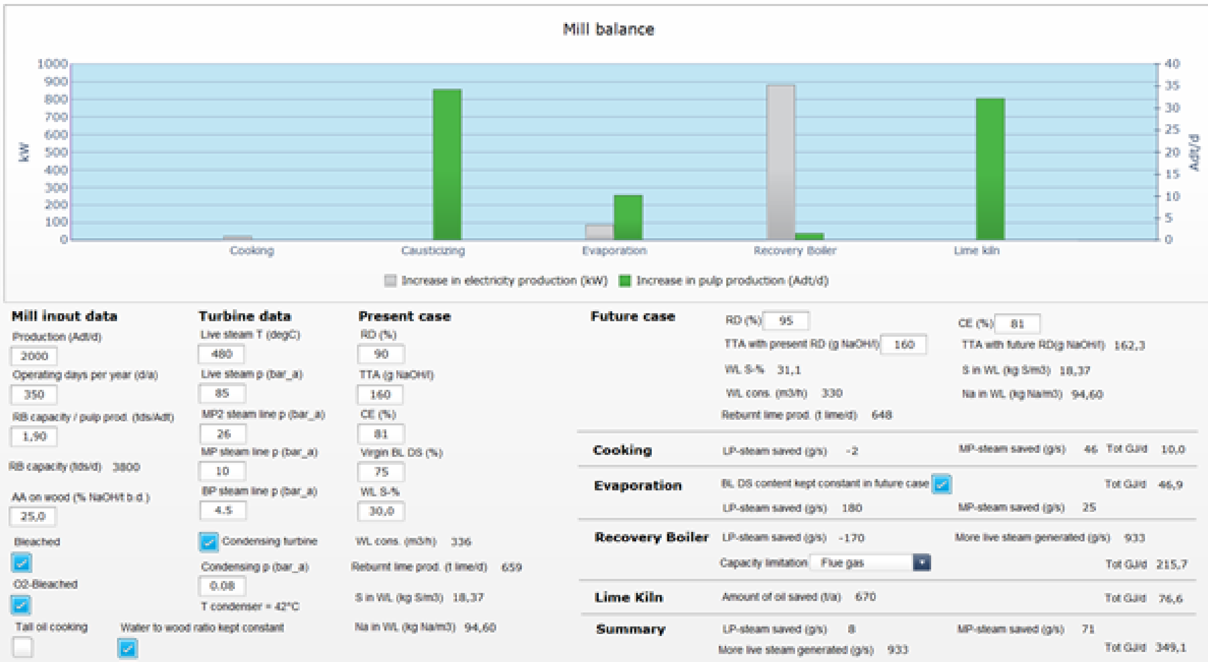


***Figure 5. Potential increase in electricity production and/or pulp production due to higher reduction rate.***

**Figure 6** shows how operational costs are changed. An electricity price of 40€/MWh, heavy fuel oil price of 300€/t and 150€/Adt production gross margin have been used in the calculations. Extra income from increased electricity production and oil savings in the lime kiln give more than 500 000€/a. Debottlenecking the evaporation plant leads to similar extra income and debottlenecking the causticizing/lime kiln yields up to 1.8M€/a.


***Figure 6. Potential increase in OPEX due to higher reduction rate.***

## Conclusions

During the test and commissioning period it was discovered that reduction rate depends on numerous control variables. When different boiler process data sets were studied, it became clear that reduction rate correlations with each running parameter vary significantly. As in any recovery boiler optimization project, finding these highest correlations is the first step in creating the control strategy.

Frequent and fully automated analysis of the reduction rate improves the result of reduction rate control and optimization dramatically. Because accurate and reliable reduction rate modelling, utilizing process variables is very challenging or even impossible to carry out, frequent automated reduction rate results as feedback is most practical for control purposes.

During the test period, it was determined that the theory of chemical reduction rate process was matching very well with practice. Still, the boiler's own characteristics play a strong role in finding the correct control parameters. In addition, bed size is also a significant variable in stabilizing reduction rate results.

The test run period and further long term reduction rate control results are excellent. Very low reduction variability and actual feedback from the Valmet Recovery Liquor Analyzer continuously follow the operator's set point. Overall performance of the liquor analyzer has proven to be equally flawless. The fact that this is most likely the first recovery boiler in the world where a fully automated control solution is managing the reduction rate increases the significance of the results.

A high reduction rate has a significant positive impact to the entire liquor recovery cycle. It supports maximized production and energy efficiency of the pulp mill, due to stronger white liquor concentration and higher black liquor heat value. An optimized recovery boiler with reduction rate control can now maintain high energy efficiency targets in variable process circumstances.

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*This white paper combines technical information obtained from Valmet personnel (Timo Laurila, Jarmo Mansikkasalo and Mikko Leskinen) and published Valmet articles and papers.*

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