Chemical pulping

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Effect of polysulfide pulping process on the energy balance of softwood and hardwood kraft pulp mills

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Abstract: Polysulfide pulping is a method to increase the pulp yield in a kraft pulp mill. Higher production is in the core of pulp mill process development, but modifications in cooking raise questions on their effects on the other parts of the process. This study focuses on the impacts of polysulfide pulping on the energy use and production of kraft pulp mills. The impacts are estimated by calculating and analyzing the steam and electricity balances of reference softwood and hardwood mills. Energy generation using residual biomass is an essential part of the operation of a kraft pulp mill, and often a notable source of income. The results show that implementation of polysulfide cooking affects both energy consumption and production. Higher hemicelluloses content of pulp cooked using polysulfide liquor means that less organic material ends up in the black liquor. Subsequently, the recovery boiler energy production suffers. The reduced steam production together with increased steam consumption decreased electricity production, corresponding to a decline in sellable electricity of 22.4 % in the hardwood mill and 28.4 % in the softwood mill. The study shows that increasing the pulp production by investing in polysulfide cooking in standalone kraft pulp mills can be economically feasible.

Keywords: bioenergy; kraft pulp mill; polysulfide pulping; process efficiency; pulp yield.

Introduction

The primary advantage of polysulfide (PS) pulping is the increase of pulp yield. Carbohydrate loss during the cooking process is one of the main drawbacks of the traditional kraft pulping process. Lower wood usage for the same production leads to higher cost-effectiveness, especially when larger amount of sellable pulp can be produced using less feedstock and chemicals. Pulp yield can increase about 1–3 % when polysulfide, anthraquinone (AQ), or both are used (MacLeod 2007). In addition to yield increase, polysulfide pulping enables a lower kappa number without yield loss, which allows a reduction in the use of bleaching chemicals (Colodette et al. 2001, Dobson and Bennington 2002, Tench et al. 1999).

Polysulfide cooking is not commonly used, although the technology has been available for long (Kleppe and Minja 1998). Growing demand for more efficient processes can be expected to increase the interest in polysulfide pulping in the near future. Energy efficiency is in the core of the development of kraft pulping process, process scale-up and environmental concerns as an obvious part of the progress. Implementation of the polysulfide process affects the pulp quality as well as the pulping process. Effect on for instance pulp strength, recovery cycle operations, corrosion, and costs have been matters of concern (Colodette et al. 2001, Kleppe and Minja 1998). These concerns can be addressed by publishing practical experiences from operating units and research results on the impacts of the technology.

Previous studies agree that polysulfide process increases the pulp yield (Copur and Tozluoglu 2008, Hakainen and Teder 1997, Jiang et al. 1994, Luthe and Berry 2005, MacLeod 2007, Vaaler and Moe 2001). The yield increase is based on retention of higher amount of hemicelluloses in pulp, because polysulfide compounds decrease the dissolution of hemicelluloses in cooking. Consequently, less hemicelluloses end up in the recovery boiler with black liquor, which reduces the dry solids load of the boiler. When the recovery boiler is the bottleneck of the pulping process, polysulfide pulping can be used to increase the pulp production without need for expensive...
modifications to the boiler. Lower amount of organics in the black liquor decreases steam generation in the recovery boiler. This leads to decrease in electricity generation.

This study aims at a deeper understanding on the effects of polysulfide pulping on the energy balance of a modern large eucalyptus kraft pulp mill. Previous studies on PS cooking have focused on the chemistry of the process as well as the impacts on the pulp quality primarily in softwood (SW) mills. PS process has been utilized in softwood mills, but there is a lack of published practical experience from eucalyptus kraft pulp mills. The objective of this study is to estimate how implementation of PS changes the steam and electricity balances of the reference mill producing kraft pulp using eucalyptus wood. The study is made by utilizing mill measurements to model the changes in the processes of a reference softwood mill and then utilizing these changes in a hardwood (HW) mill model. Based on the results and earlier studies, the advantages and drawbacks of the implementation are discussed. Economic analysis is made by calculating payback periods for polysulfide cooking investments to evaluate economic feasibility.

Materials and methods

Energy generation in a modern kraft pulp mill

A modern kraft pulp mill produces heat and power by combusting residual biomass from its own processes. Typically, modern pulp mills are energy-independent apart from fossil fuels used in lime kilns and during start-up, shutdowns, and upsets. Heat and power are often produced in excess of own requirements (Vakkilainen and Kivistö 2014). Bio-based heat or power sale is an additional source of income for many pulp mills.

Steam is generated in the recovery boiler, where black liquor is combusted as a part of the chemical circulation of the pulping process. In many mills, especially in Northern Europe, there is also a power boiler where bark and residual biomass from the wood handling process is combusted for additional steam generation. Steam is used in the pulping process for heating purposes as well as in a steam turbine for power generation. The efficiency of steam use in the mill processes affects the amount of electricity for sale, because excess steam can be used to increase condensing power generation. Power is needed in the mill processes, but typically in modern mills, it is generated in excess of own requirements. The surplus is often sold or used in an integrated paper mill. Changes in the efficiency of steam production or consumption will affect the mill’s operational costs.

Polysulfide pulping process

Polysulfide pulping as a method to increase pulp yield has been known since the 1940’s (Kleppe and Minja 1998). Polysulfides, such as Na$_2$S$_2$ or Na$_2$S$_3$, decrease hemicellulose degradation in the early stage of cooking, when temperature range is from 100 °C to 120 °C and profuse dissolution of hemicelluloses occurs (Gustafsson et al. 2011). Pulp yield increases due to larger amount of hemicelluloses in pulp (Gellerstedt 2009). The yield increase results mostly from retention of hemicelluloses, but also from protection of cellulose chains (Colodette et al. 2001). Polysulfide compounds stabilize especially glucomannan and xylan when used in softwood pulping (Copur and Tozluoglu 2008). In eucalyptus pulping tests, half of the yield increase was found to result from xylan content increase, while in pine pulping the majority of yield gain resulted from retention of mannans (Colodette et al. 2001).

Along with higher yield, increased capacity of the recovery boiler due to lower black liquor amount is included in the benefits of polysulfide pulping. The recovery boiler is often the bottleneck of the kraft pulping process. Polysulfide pulping can be seen as a way to increase production without expensive retrofit to the recovery boiler. On the other hand, decreased amount of organics in black liquor will lead to decrease in steam and power generation.

The implementation of polysulfide pulping includes both the production of polysulfide that changes the properties of the alkaline cooking liquor and modifications in the cooking process to enable the maximum utilization of polysulfide. Polysulfide can decompose to thiosulfate if temperature or pH is too high and therefore changes in the cooking temperature profile are usually required (Szepaniak 2014). However, some mills have been able to operate using existing cooking parameters when changing to PS cooking (Hara 1991). The quality of pulp is one of the main issues whenever the PS pulping process is used. Minor changes in the pulp composition or quality have been noticed in earlier studies on polysulfide pulping (Copur and Tozluoglu 2008). The studies show that pulp tear strength may be affected due to higher hemicellulose content, but it can typically be expected to meet customary requirements. Increased hemicellulose content in PS pulp typically leads to better beatability (Hakanen and Teder 1997). Therefore, beating energy consumption of polysulfide pulp to given tensile index can be expected to be lower.
In polysulfide pulping, white liquor oxidation is used to convert a part of sulfide sulfur into elemental sulfur. The PS cooking liquor is called orange liquor due to its color in comparison with white liquor in traditional cooking process (Hakanen and Teder 1997). The most used industrial polysulfide generation method is the Moxy (Mead Oxidation) process that was first implemented in the year 1973 in Mead Corporation Chillicothe mill (Kurittu 1998). The Moxy process is a partial oxidation process of white liquor, where clarified white liquor is filtered and led to a reactor. There the sulfide is oxidized and converted to polysulfide sulfur in the presence of carbon catalyst (Kleppe and Minja 1998). In the reactor, 60 % to 70 % of sodium sulfide (Na$_2$S) oxidizes, of which approximately two thirds forms polysulfide while one third reacts to form thiosulfate and caustic, following reactions 1 and 2 (Arpalahti et al. 2008).

$$4 \text{Na}_2\text{S} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{S}_2 + 4\text{NaOH} \quad (1)$$

$$2\text{Na}_2\text{S} + 2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH} \quad (2)$$

Other commercial polysulfide processes are Chiyoda and Paprilox, which bear resemblance to the Moxy process (Eriksson and Bennington 2003, Kleppe and Minja 1998, Luthe and Berry 2005, Tench et al. 1999). Chiyoda process uses carbon as catalyst. To increase the lifetime of the catalyst, white liquor filtration is required before the reactor, as well as in the Moxy process (Kleppe and Minja 1998). Paprilox process is another catalytic white liquor oxidation process, and it can be retrofitted into an existing causticizing system (Luthe and Berry 2005, Tench et al. 1999). It is also possible to produce polysulfide using electrochemical oxidation (Watanabe et al. 2001). In this electrolytic process, white liquor is oxidized at anode to produce polysulfide, and NaOH is generated at cathode. High PS concentrations can be reached using electrolytic process.

**Reference mill processes and operation**

In this study, two reference mills are modelled to analyze the effects of polysulfide pulping on the steam and power balances of the mills. The studied reference mills are:

- **Mill A**: A modern softwood kraft pulp mill located in Northern Europe, pulp production 600 000 ADt/a
- **Mill B**: A modern eucalyptus kraft pulp mill located in South America, pulp production 1 500 000 ADt/a

The mass and energy balances of the reference mills have been calculated using an updated *MillFlow* program. *MillFlow* is a mill spreadsheet that has been introduced in more detail in earlier studies (Hamaguchi et al. 2011, Kuparinen 2019, Vakkilainen and Kivistö 2008). The model Mill A is updated from a model that was used in an earlier study where it was checked against actual mill operation (Vakkilainen and Kivistö 2008). Mill B was introduced in more detail in previous studies (Hamaguchi et al. 2011, Ku-
Implementation of polysulfide pulping to the reference mill operations

Figure 1 presents a simplified block diagram of a pulp mill including a polysulfide process. The implementation of the polysulfide process requires installation of a white liquor clarification process and the actual PS reactor. Also changes in piping and process optimization, especially in cooking, are needed.

The polysulfide process was modelled using literature data (Hara 1991, Jiang et al. 1994, Nishijima et al. 1995) and vendor data. The effect of PS on the softwood mill operation was compared with the literature and mill operating data. The experience from softwood mill model was utilized with the PS eucalyptus mill model.

PS concentration in orange liquor varies from mill to mill. It was set at 5 gS/l for both studied mills based on literature. Pulp yield increase in the SW mill was 1% based on the actual mill data. The previous experiments have suggested yield increases up to 3% (Demuner et al. 2020) or even higher with a large dosage of sulfur (Copur 2007). The relatively low yield increase in the example mill resulted from the already high yield before PS cooking and the requirement to retain pulp strength. In previous trials, PS process was shown to increase the pulp yield also in eucalyptus pulp mills (Colodette et al. 2001). Based on laboratory experiments (Demuner et al. 2020, Zanão et al. 2019) and reported trials producing eucalyptus pulp using PS process and the knowledge on SW pulp processes, the yield increase was estimated at one percentage unit also in the HW mill case. For eucalyptus mill, there is a lack of published data of mill trials, but the used 1% yield increase is a reasonable estimate of a possible industrial level. In an existing mill, this increase can be estimated observing the changes in the amounts of produced pulp and generated steam. Varying moisture content of incoming wood makes accurate measurements of utilized wood challenging in the mill environment.

Orange liquor concentration differs from that of white liquor. Based on experiences on Japanese mills, the amount of active alkali decreases while the amount of effective alkali increases (Nishijima et al. 1995). Also sulfidity is typically low. The composition of orange liquor was calculated using white liquor from base case mills which oxidizes according to reactions (1) and (2) so that the targeted polysulfide concentration is achieved.
Polysulfide pulping increases the amount of pulp, which causes a decrease in the organics to be burned in the recovery boiler. In the studied cases, wood input was kept the same, which means an increase in pulp production. The decrease in the load of the recovery boiler means lower amount of combustion air and consequently, lower flue gas flow and lower specific emissions per ton of product, if the flue gas emissions can be kept the same.

It can be assumed that PS does not affect the fate of the inorganic matter in the cooking liquor. The organic/inorganic relation changes, as the amount of organics in black liquor decreases and the amount of inorganics remains stable. This may change the heating value of black liquor. In practice, the heating value has been found to decrease, but the change is small (Parkko 2013). The change in the dry matter of the black liquor is more significant. Other effects on the combustion operations include e.g. possible increase in SO₂ emissions from the recovery boiler, because polysulfide process increases the amount of reactive sulfur in black liquor. In long-term use, SO₂ causes corrosion in the boiler equipment. In mills where PS process has been used, neither higher sulfur emissions nor increased corrosion have been reported.

The viscosity of black liquor from polysulfide cooking is typically slightly lower than that of traditional black liquor, which can make the evaporation process easier (Hara 1991). The changes in BL composition can lead to fouling of evaporator and therefore in a mill trial, a more frequent need for washing (Szepaniak 2014). In addition to the changes in the chemical cycle, PS cooking may affect bleaching and drying. Possible changes in residual lignin might affect bleaching chemical consumption and steam usage. PS pulp most probably means changes in the operation of drying machine, and in its steam consumption. If the required dryer capacity exceeds the nominal capacity, an increase in the drying steam pressure or an additional infrared drying equipment is often required.

Results and discussion

Polysulfide pulping can be used to increase pulp yield in kraft pulp mills. Utilization of PS affects the mill operations, including the mass and energy balances of the mill. Based on literature data, the implementation and effects of PS in a softwood kraft pulp mill were modelled using MillFlow Excel spreadsheet. The results were compared with literature data. The model was then used to estimate the effects of PS in an eucalyptus pulp mill.

When polysulfide pulping is implemented in an existing pulp mill, the process is optimized to gain the maximum benefit from the changes. Some of the changes in reported trials and experiences from existing mills may result from other simultaneous modifications in addition to the actual PS process. This should be considered when the reported results are used to estimate the effects of the PS process.

Softwood mill results

The results of the softwood mill calculations using MillFlow are largely consistent with earlier results in literature and mill trials. The main process values before and after PS implementation are collected in Table 2. The chosen PS concentration of 5 gS/l in the produced orange liquor led to increase of one percentage unit in pulp production, namely from 45 % to 46 %. When wood input was kept the same in both cases, pulp production increased 2.0 %. The cooking liquor flow per produced pulp ton decreased due to different composition of the cooking liquor, but the daily use of cooking liquor remains the same because of the increased yield.

The changes in cooking affect the recovery cycle. In the example mill, changes in the washing stage were implemented at the same time with the polysulfide cooking project. The improved washing increased the dry solid content of weak black liquor, which can be seen as a decreased load in the evaporators. The load decreased 3.5 % from 566 tH₂O/h to 546 tH₂O/h, and the heat consumption per pulp ton was 5.6 % lower in the PS pulping case. The results suggest that mill’s power consumption is lower when PS pulp is produced compared with traditional kraft pulping, mainly due to decreased evaporator load.

The amount of organic material ending up in BL from cooking decreased as expected, which can be seen as a reduced heating value (~0.8 %). Daily black liquor flow remained practically the same but the black liquor flow per produced pulp ton decreased. The changes in the BL flow led to a steam production decrease of 3.2 %. Only few of the earlier trials have reported the change in steam production. The decrease was approximately 4 % at Hachinohe mill (Hara 1991). Munro et al. (2002) reported 8.3 % increase in steam production per BL dry solids. A small increase (2.7 %) in the dry solid content of black liquor was reported but the result is nonetheless unexpected. Electricity is produced using excess steam. Less excess steam is available after PS implementation due to the lower steam
Table 2: The main process values of the SW mill in the base case and after the implementation of the PS process.

| Production                          | Unit     | SW mill, base case | SW mill, PS case | Change   |
|-------------------------------------|----------|--------------------|-----------------|----------|
| Operating hours                     | h/a      | 8400              | 8400            | 0.0 %    |
| Bleached pulp production            | ADt/a    | 600000            | 613334          | 2.2 %    |
| Wood handling                       |          |                    |                 |          |
| Wood required                       | m³ sob/d | 7960              | 7960            | 0.0 %    |
| Residue generated                   | BDt/d    | 607               | 607             | 0.0 %    |
| Cooking                             |          |                    |                 |          |
| Yield                               | %        | 45                | 46              | 2.2 %    |
| Polysulfide concentration           | gS/l     | –                 | 5               | –        |
| White liquor flow to digester       | m³/d     | 6485              | 6485            | 0.0 %    |
| White liquor dry solids             | %        | 13.9              | 14.4            | 3.0 %    |
| White liquor sulfidity              | %        | 38.7              | 26.3            | –32.4 %  |
| Active alkali charge as Na₂O        | %        | 17.5              | 16.2            | –7.2 %   |
| Active alkali as NaOH               | gNaOH/l  | 129               | 120             | –7.2 %   |
| Effective alkali as NaOH            | gNaOH/l  | 104               | 104             | 0.0 %    |
| Causticity                          | %        | 84                | 84              | 0.0 %    |
| Kappa after cooking                 | –        | 30                | 30              | 0.0 %    |
| Recovery boiler and evaporator      |          |                    |                 |          |
| Evaporator load                     | tH₂O/h   | 566               | 546             | –3.5 %   |
| Black liquor dry solids flow        | tDS/ADt  | 1.93              | 1.89            | –2.1 %   |
| HHRR (boiler load)                  | MW/m²    | 2.85              | 2.83            | –0.7 %   |
| Black liquor HHV                    | MJ/kgDS  | 13.97             | 13.87           | –0.8 %   |
| Net steam flow                      | t/h      | 454               | 449             | –1.0 %   |
| RB steam/BL solids virgin           | kg/kg    | 3.44              | 3.40            | –1.1 %   |
| Steam generation                    | MJ/ADt   | 21350             | 20670           | –3.2 %   |
| Reduction                           | %        | 95                | 95              | 0.0 %    |
| RB flue gas                         | NM³/ADt  | 6743              | 6601            | –2.1 %   |
| Organics in BL                      | %        | 69.8              | 68.9            | –1.2 %   |
| Reduction                           | %        | 95                | 95              | 0.0 %    |
| Heat consumption                    |          |                    |                 |          |
| Cooking                             | MJ/ADt   | 2780              | 2980            | 7.2 %    |
| Bleaching                           | MJ/ADt   | 870               | 1150            | 32.2 %   |
| Evaporation                         | MJ/ADt   | 5199              | 4909            | –5.6 %   |
| Drying                              | MJ/ADt   | 2410              | 2580            | 7.1 %    |
| Recovery boiler                     | MJ/ADt   | 1780              | 1790            | 0.1 %    |
| Miscellaneous                       | MJ/ADt   | 1168              | 1157            | –0.9 %   |
| Steam consumption, total            | MJ/ADt   | 14210             | 14570           | 2.5 %    |
| Electricity                         |          |                    |                 |          |
| Steam for power generation          | MJ/ADt   | 3697              | 3406            | –7.9 %   |
| Power generation                    | MW       | 69                | 65              | –5.8 %   |
| Power consumption                   | kWh/ADt  | 739               | 731             | –1.1 %   |
| Excess power for sale               | MW       | 16                | 12              | –28.4 %  |

generation and increased steam consumption, and therefore electricity production decreases. Electricity generation decreased 5.8 %, which led to 28.4 % decrease in sellable electricity. However, the example mill can still cover its electricity demand by own production.

Combustion air requirement depends on the amount of organic material of fuel. Decreased air flow into the recovery boiler in relation to BL flow indicates that the amount of organic matter in BL has decreased. Change in combustion air flow leads to change in the amount of flue gas. Flue gas production per pulp ton decreased 2.1 %. Absolute flue gas flow did not change notably due to increased pulp production. Emissions in relation to production decrease because less energy per pulp ton is produced. Formation of some emissions such as SO₂ are out of the focus of this study.
Eucalyptus mill results

The effects of adopting polysulfide pulping in the reference eucalyptus pulp mill were studied by modelling the process using the MillFlow Excel spreadsheet. The model is based on the earlier model on South American eucalyptus pulp mills. The PS process changes were based on the effects in mills as reported in mill trials and literature studies as well as the reference SW model used in this study. Table 3 shows the process values of the eucalyptus mill in the base case and after PS implementation, based on the MillFlow calculations.

Properties of the cooking liquor change when polysulfide cooking is implemented. Active alkali decreases notably whereas effective alkali remains unchanged. Less active alkali is needed for cooking, and white liquor dry solids content increases. There is practically no change in the cooking liquor flow for unit of wood used. Less liquor is needed per produced pulp ton because the total production has increased. Changes to cooking are similar with the case of softwood mill. It was assumed that pulp drying capacity was adequate to handle the additional pulp production without modifications.

Effects of PS cooking on the evaporator operation differ from the softwood mill case. In the reference softwood mill, washing stage was renovated, which affected notably on the dry solids content of the weak black liquor. It was assumed that washing is not modified in the hardwood mill case. The evaporator load increased 1.1% because of slightly increased weak black liquor flow. However, the steam consumption of evaporator per produced pulp ton decreased 0.7%.

Higher heating value of black liquor decreased 0.7% due to the lower share of organics in the dry solids of black liquor. Black liquor dry solids flow per pulp ton decreased 2.0% due to less organics ending up in the black liquor. The decreased heating value and lower flow of organics to recovery boiler led to a decrease of 1.1% on the net steam flow. Therefore, even if the heat production per ton of pulp decreased 2.9%, the implementation of PS cooking did not have a great effect on the absolute steam production. Increased production and decreased organics in the black liquor led to decrease of 2.0% in recovery boiler’s flue gas flow per produced pulp ton. Absolute amount of flue gases changed only slightly.

The results suggest that total steam consumption increases 4.7% Together with the lower steam generation, the increased consumption led to a decrease in electricity production. The power generation dropped 6.2%. Mill’s power consumption did not change significantly. Excess power for sale decreased 22.4%. In the case of southern hardwood mills, it should be noted that excess power may not be a valuable product due to lack of distribution network.

Economic analysis and discussion on the feasibility

The economic analysis was made by calculating a payback period for polysulfide process investment for both Nordic softwood mill and Southern hardwood mill. The key variables were prices for electricity, pulp, and wood. Selling electricity can be a notable source of income especially in the case of Northern softwood mill. As both mills are energy self-sufficient, changes in energy consumption affect only the amount of excess electricity. Expected yield increase from running the polysulfide process leads either to saving in wood input or increase in pulp production. Investment cost of 15 Me is used for the softwood mill (Partanen 2012). The cost is scaled for the hardwood mill using Equation (3).

\[
\frac{C}{C_{ref}} = \left( \frac{M}{M_{ref}} \right)^n \tag{3}
\]

where C stands for investment costs and M for capacity of a mill. Scaling factor n is 0.67 in this study. The capacity and the investment cost of the SW mill are used as a reference. Used values for the lifetime of the investment and interest rate are 25 years and 7%, respectively. The annual operation and maintenance costs of the PS process are estimated at 5% of the investment. Based on the chemical balance of the mill and costs presented in Onarheim et al. (2017), cost for additional bleaching chemicals in case of increased pulp production was set at 35 e/ADt. Other minor variables such as changes in water use or effluents were excluded.

The results show that if the polysulfide process is used for increasing the pulp production, the investment is economically feasible in most of the cases (Figure 2). Some previous trials have reported yield increases up to 3% for softwood mills, and therefore two additional cases for higher yield increase (2%) were calculated. If the higher yield increase can be reached, the payback period drops significantly. Electricity price affects the payback period if it is assumed that the excess electricity is a source of income for the mill. It should be noted that especially in remote areas electricity cannot be always sold. This is the case in many southern hardwood mills that have no or only a restricted access to the national distribution network. The economic analysis highlights the fact that polysulfide cooking should be used for increasing the pulp production instead of saving on wood cost.
Table 3: The main process values of the eucalyptus mill in the base case and after the implementation of the PS process.

| Production                                      | Unit | HW mill, base case | HW mill, PS case | Change |
|------------------------------------------------|------|--------------------|------------------|--------|
| Operating hours                                | h/a  | 8400               | 8400             | 0.0 %  |
| Bleached pulp production                       | ADt/a| 1500000            | 1528300          | 1.9 %  |
| Wood handling                                  |      |                    |                  |        |
| Wood required                                  | m³ sob/d | 16710              | 16710            | 0.0 %  |
| Residue generated                              | BDt/d| 1274               | 1274             | 0.0 %  |
| Cooking                                        |      |                    |                  |        |
| Yield                                          | %    | 53                 | 54               | 1.9 %  |
| PS concentration in WL                         | gS/l | –                  | 5                | –      |
| White liquor flow to digester                  | m³/d | 12242              | 12245            | 0.0 %  |
| White liquor dry solids                        | %    | 15.6               | 16.0             | 2.5 %  |
| White liquor sulfidity                         | %    | 32.0               | 20.1             | −37.1 %|
| Active alkali charge as Na₂O                   | %    | 17.1               | 15.9             | −6.6 % |
| Active alkali as NaOH                          | gNaOH/l | 140                | 131              | −6.6 % |
| Effective alkali as NaOH                       | gNaOH/l | 118                | 118              | 0.0 %  |
| Kappa after cooking                            | –    | 18                 | 18               | 0.0 %  |
| Causticity                                     | %    | 83                 | 83               | 0.0 %  |
| Recovery boiler and evaporator                 |      |                    |                  |        |
| Evaporator load                                | tH₂O/h | 1286               | 1301             | 1.1 %  |
| Black liquor dry solids flow                   | tDS/ADt | 1.46               | 1.43             | −2.0 % |
| HHRR (boiler load)                             | MW/m² | 3.43               | 3.41             | −0.8 % |
| Black liquor HHV                               | MJ/kgDS | 13.65              | 13.55            | −0.7 % |
| Net steam flow                                 | t/h  | 859                | 850              | −1.1 % |
| RB steam/BL solids virgin                      | kg/kg | 3.54               | 3.42             | −3.4 % |
| Heat generation                                | MJ/ADt | 16280              | 15810            | −2.9 % |
| RB flue gas                                    | Nm³/ADt | 5590               | 5478             | −2.0 % |
| Organics in BL                                 | %    | 65.2               | 64.3             | −1.3 % |
| Reduction                                      | %    | 94                 | 94               | 0.0 %  |
| Steam consumption                              |      |                    |                  |        |
| Cooking                                        | MJ/ADt | 1829               | 1960             | 7.2 %  |
| Bleaching                                      | MJ/ADt | 580                | 767              | 32.2 % |
| Evaporation                                    | MJ/ADt | 2988               | 2966             | −0.7 % |
| Drying                                         | MJ/ADt | 2100               | 2248             | 7.1 %  |
| Recovery boiler                                | MJ/ADt | 977                | 963              | −1.4 % |
| Miscellaneous                                  | MJ/ADt | 707                | 706              | −0.1 % |
| Steam consumption, total                       | MJ/ADt | 9180               | 9611             | 4.7 %  |
| Electricity                                    |      |                    |                  |        |
| Steam for power generation                     | MJ/ADt | 3380               | 3113             | −7.9 % |
| Power generation                               | MW   | 157                | 147              | −6.2 % |
| Power consumption in mill                      | kWh/ADt | 602                | 598              | −0.6 % |
| Excess power for sale                          | MW   | 49                 | 39               | −22.4 %|

The mill type affects the feasibility of the polysulfide process. Integrated pulp and paper mills require more heat and electricity than stand-alone mills, and typically they are not energy self-sufficient. Therefore, decrease in steam and electricity production due to implementation of polysulfide cooking leads to increasing demand for purchased energy and can thus decrease the attractiveness of the investment.

Polysulfide cooking has several effects on the kraft cooking. Many of them are attractive but also some drawbacks have been documented. The results of previous studies including the current study are collected in Table 4. The purpose of PS cooking is to increase yield, and the studies agree that the PS addition leads to higher yield, but the magnitude of the increase varies within different wood species, polysulfide and anthraquinone charges, and cooking conditions. General opinion is that the PS cooking can be used for decreasing kappa number without impairing the yield, but a few studies have documented increased kappa numbers. Copur (2007) suggested that...
increased kappa number may be a result of high sulfidity. Most of the studies found that PS pulping increases tensile and burst index while tear index reduces. However, Demuner et al. (2020) did not observe any changes in physical, chemical, or morphological properties. Some studies, for instance (Kleppe and Minja 1998), also stated that the reduce in tear strength is usually not harmful for paper making.

Only few studies have investigated the effect of PS cooking on the recovery cycle, energy production, and energy consumption. The current study provides detailed information of the effects of PS cooking on the energy use and production in Northern softwood and Southern hardwood pulp mills. The findings are in line with the previous results. Employing PS cooking increased steam demand and reduced energy production but did not lead to demand for additional steam production in the studied mills. The results suggest that revenues from increased pulp production can easily cover losses from reduced electricity production and capital costs.

PS cooking has not become a popular cooking method even though it has been known approximately eight decades and a few mills have reported encouraging experiences. As there seems to be no crucial barriers, it is possible that increasing demand for high material efficiency will promote the adoption of PS cooking in the future.

**Conclusions**

This study evaluated the implementation of polysulfide cooking in a modern hardwood mill based on its perfor-
The economic analysis shows that the profits from the increased pulp production are notably higher than losses from the decreased energy production, and therefore polysulfide cooking can be economically feasible. No crucial drawbacks in polysulfide pulping have been reported. Thus, implementation of polysulfide cooking in kraft pulp mills seems practical. However, changes in the pulp quality may be an issue for some mills, and if the polysulfide cooking is implemented in mills with high energy consumption, for instance in integrated pulp and paper mills, maintaining the energy supply can be a concern. As there are no modern large eucalyptus polysulfide kraft pulp mills operating currently, the detailed verification of the hardwood polysulfide processes of this study might be addressed in future studies.

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