

# The Feasibility of Utilizing Existing Process Streams in Kraft Pulp Mills as a Source of Chemicals for Lignin Extraction

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Lignin is a sustainable raw material with a high potential for use in the production of renewable products. While the market for lignin is slowly growing, lignin recovery *via* acid precipitation during the kraft pulping process requires the addition of chemicals that will impact the chemical balance of the pulp mill. This negatively affects both the environmental and business operations. Utilizing existing process streams as a source of chemicals will allow the mill to close the chemical loop and reduce emissions, which will have positive environmental impacts. This study investigated the internal production of sulphuric acid ( $H_2SO_4$ ) and carbon dioxide ( $CO_2$ ) for use in lignin separation (also called extraction) at a Swedish kraft pulp mill. The process simulation tool CHEMCAD was used to model and analyze the wet gas  $H_2SO_4$  (WSA) process to produce  $H_2SO_4$ . The chemical absorption process using monoethanolamine (MEA) to capturing  $CO_2$  was also analyzed. The utilization of the sulphur-containing gases to produce  $H_2SO_4$  can generate an amount that corresponds to a significant lignin extraction rate. The  $CO_2$  available in the flue gases from a mill well exceeds the amount required for lignin extraction.

*Keywords:* Lignin removal; Sulphuric acid;  $CO_2$ ; Chemical absorption; MEA; WSA; CHEMCAD

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## INTRODUCTION

The forest industry and pulp mills will play an important part in the transition towards a sustainable bioeconomy, as pulp mills have good prerequisites to produce sustainable and renewable products. Lignin is a molecule having a high potential for use in the production of advanced biofuels and renewable chemicals (Norgren and Edlund 2014; Dessbesell *et al.* 2020). The implementation of a lignin extraction process in an existing pulp mill will increase the consumption of various resources, such as steam, water, and chemicals (Benali *et al.* 2014).

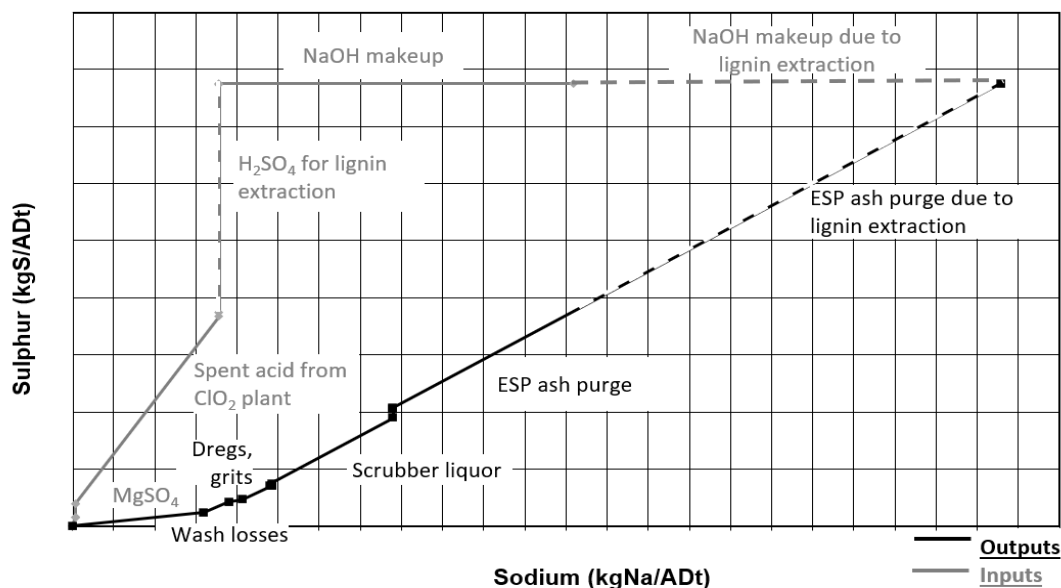
The conditions for lignin recovery vary among different pulp mills. Each pulp mill is unique and has its own set-up and energy balance. However, one commonality for all pulp mills is that lignin extraction will have an impact on the mass and energy balance of the facility. The influence of lignin extraction in kraft pulp mills has been investigated in several studies (Hamaguchi *et al.* 2011; Périn-Levasseur *et al.* 2011; Kannangara *et al.* 2012; Benali *et al.* 2014; Kihlman 2016).

Lignin separation *via* acid precipitation is the most developed and widely implemented process (Hubbe *et al.* 2019). This process requires the addition of acidifying agents, preferably carbon dioxide ( $CO_2$ ) and sulphuric acid ( $H_2SO_4$ ). Depending on their

origin, each of these acidifying agents generates emissions of greenhouse gases with varying amounts of global warming potential (GWP) (Wells *et al.* 2015). The lignin extraction processes are straightforward. Chemicals, in the form of  $\text{CO}_2$  and  $\text{H}_2\text{SO}_4$ , are purchased and added to the pulp mill's chemical balance. The lignin is removed, and the excess chemicals must be extracted to preserve the chemical balance. The cost of the acidifying agents and the make-up chemicals required is one of the main parameters that affect the profitability of the lignin extraction process.

The liquor cycle in kraft pulp mills is becoming increasingly closed because of stricter environmental limits and economic incentives to minimize the need for make-up chemicals. The sodium/sulphur (Na/S) balance in pulp mills is important to enable the stable operation to control the costs of make-up chemicals. To manage the Na/S balance, many mills purge electrostatic precipitated (ESP) ash. Although the ESP ash consists primarily of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), it also contains sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). The Na/S balance is often visualized as a vector diagram that shows the input and output of the sodium and the sulphur as kg per ADt (Air-dry metric tons) of pulp. Figure 1 shows the effect of the lignin extraction *via* acid precipitation using  $\text{H}_2\text{SO}_4$  schematically. The addition of sulphur disrupts the mill's Na/S balance, so the sulphur output needs to be increased, *e.g.* by purging ESP ash. Increasing the sulphur output *via* such purging will also increase the need for sodium make-up. As illustrated in Fig. 1, the addition of  $\text{H}_2\text{SO}_4$  in the lignin extraction process has a large impact on the mill's Na/S balance.

Due to economic and environmental reasons, kraft pulp mills are under increasing pressure to reduce the amount of purged sodium and sulphur they release as effluent (Valeur *et al.* 2000). The purging of salt into the environment is expected to become an issue in the future, as more stringent environmental regulations could lead to limited rights for the emissions of salt.



**Fig. 1.** The vector diagram of Na/S, with lignin removal *via* acid precipitation, corresponding to a lignin extraction rate of approximately 45,000 t lignin/year in the reference mill (Kihlman 2016). The solid lines represent the input and output streams that contain sodium and/or sulphur in the existing mill. The dashed lines represent the input and output streams that contain sodium and/or sulphur linked to the extraction of lignin.

The internal production of H<sub>2</sub>SO<sub>4</sub> would reduce the need for bleeding ESP ash to maintain the Na/S balance. The Metsä Group's bioproduct mill in Äänekoski, Finland, which started up in 2017, is an example of this process. Thanks to the mill's internal H<sub>2</sub>SO<sub>4</sub> production plant, the sulphate emissions (*via* the purging of ESP ash) into waterways are minimized. Despite a production volume that is almost triple that of the old pulp mill in Äänekoski, the new pulp mill can operate within the same emission limits stated in the old environmental permit and wastewater conditions (Metsä Fibre 2020).

Sulphuric acid is one of the most widely used chemicals in the world. Over 250 million tons of H<sub>2</sub>SO<sub>4</sub> is produced every year, primarily for use within the fertilizer industry. The raw material for H<sub>2</sub>SO<sub>4</sub> is sulphur dioxide (SO<sub>2</sub>) gas, where burning elemental sulphur is the most common way to produce SO<sub>2</sub>. Industrial waste gases, such as SO<sub>2</sub>, hydrogen sulphide (H<sub>2</sub>S), carbonyl sulphide (COS), and carbon disulfide (CS<sub>2</sub>), are also sources to produce H<sub>2</sub>SO<sub>4</sub> (Kjelstrup and Island 1999; King *et al.* 2013; Sørensen *et al.* 2015). Although there are several different processes to produce H<sub>2</sub>SO<sub>4</sub>, they all include the catalytic reaction of SO<sub>2</sub> with oxygen (O<sub>2</sub>) to form sulphur trioxide (SO<sub>3</sub>), and the reaction of SO<sub>3</sub> with water (H<sub>2</sub>O) to form H<sub>2</sub>SO<sub>4</sub>.

Climate change and its connection to the greenhouse gas CO<sub>2</sub> has driven the development of effective carbon sequestration. A large amount of the CO<sub>2</sub> emitted is from utility or industrial power systems (Chakravarti *et al.* 2001). In 2017, 23 of the largest pulp and paper mills in Sweden generated over 22 million tons of CO<sub>2</sub> (Andersson 2019). The capture of CO<sub>2</sub> related to the pulp and paper industry has been investigated in several different publications (Möllersten *et al.* 2003; Möllersten *et al.* 2004; Hektor and Berntsson 2007; Hektor and Berntsson 2009; Jönsson and Berntsson 2012; Onarheim *et al.* 2017). The CO<sub>2</sub> emissions from a modern pulp and paper mill, most of which is biogenic in origin, have three main sources: the recovery boiler, the lime kiln, and the power boiler. There are several different methods for CO<sub>2</sub> capture, based primarily on post-combustion, pre-combustion, and oxy-combustion technologies. All these methods aim to reduce the energy requirements and capital cost, which are costly barriers to entry for commercial implementation on a larger scale (Metz *et al.* 2005; Teir *et al.* 2010; Kalatjari *et al.* 2019).

The aim of this study was to evaluate the feasibility of utilizing existing process streams in a kraft pulp mill to enable and reduce the impact of lignin extraction by moving from a linear approach to a circular approach *via* the internal production of H<sub>2</sub>SO<sub>4</sub> and CO<sub>2</sub>. This study investigated the potential internal production rates of H<sub>2</sub>SO<sub>4</sub> and CO<sub>2</sub> and the related impact such production makes on the mill's mass and energy balance.

## EXPERIMENTAL

The reference mill in this study was a Scandinavian integrated kraft pulp and paper mill with an annual softwood pulp production capacity of 350,000 ADt and an annual paper production capacity of 165,000 tons. This mill was the same reference mill used by Kihlman (2016).

Concentrated non-condensable gases (CNCG) generated in the reference mill were collected from the fiber line, the evaporation plant, and the methanol recovery plant. These gases are normally burned in a dedicated CNCG boiler, which generates SO<sub>2</sub> and CO<sub>2</sub>, but there is also the option to burn them in the auxiliary burner or the lime kiln.

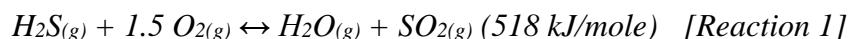
Flue gas rich in CO<sub>2</sub> is generated at four different positions at the reference mill, namely the recovery boiler, the power boiler, the lime kiln, and the CNCG boiler. The lime

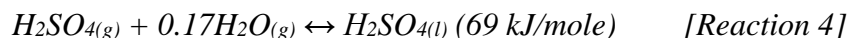
kiln uses a bio-oil, *i.e.* tall oil pitch, as a fuel and the power boiler uses biomass as the main fuel. The CNCG boiler produces significantly less flue gas than for the other three sources.

### Production of H<sub>2</sub>SO<sub>4</sub>

The use of sodium sulphide (Na<sub>2</sub>S) in the kraft pulping process means that a relatively large amount of sulphur-containing gases are generated and collected, generally as methyl mercaptan (CH<sub>3</sub>SH), dimethyl sulphide (CH<sub>3</sub>SCH<sub>3</sub>), dimethyl disulphide (CH<sub>3</sub>SSCH<sub>3</sub>), and H<sub>2</sub>S. These gases are often referred to as CNCGs. Methyl mercaptan, CH<sub>3</sub>SCH<sub>3</sub>, and CH<sub>3</sub>SSCH<sub>3</sub> are largely formed during the pulping process, whereas H<sub>2</sub>S is formed in the recovery boiler (Zhu *et al.* 2002; Sixta 2006). Methyl mercaptan is formed by the H<sub>2</sub>S ions reacting with lignin methoxyl groups, and the CH<sub>3</sub>SCH<sub>3</sub> is formed by the mercaptide ions reacting with the lignin methoxyl groups. In the presence of O<sub>2</sub>, the CH<sub>3</sub>SSCH<sub>3</sub> is formed *via* the oxidation of CH<sub>3</sub>SH (Goheen 1964; McKean *et al.* 1965; Zhu *et al.* 2002). At a lower pH level, the Na<sub>2</sub>S present in the black liquor starts to convert to H<sub>2</sub>S, which generates the H<sub>2</sub>S primarily in the evaporation plant. The H<sub>2</sub>S is also formed in the recovery boiler and in the molten smelt due to the Na<sub>2</sub>S reacting with H<sub>2</sub>O vapour and CO<sub>2</sub> (Frederick *et al.* 1996; Järvensivu *et al.* 2000). Many mills burn these sulphur-containing gases, followed by chemical absorption of the SO<sub>2</sub> generated using sodium hydroxide (NaOH) or calcium hydroxide (Ca(OH)<sub>2</sub>). Although this reduces the sulphur emissions, it requires absorption chemicals that subsequently impact the mill's operating costs. These sulphur-containing gases can instead be converted into H<sub>2</sub>SO<sub>4</sub> and remove the need for absorption chemicals. The internal production of H<sub>2</sub>SO<sub>4</sub> is also an efficient way to separate the sodium and sulphur streams, which can benefit the mill's Na/S balance.

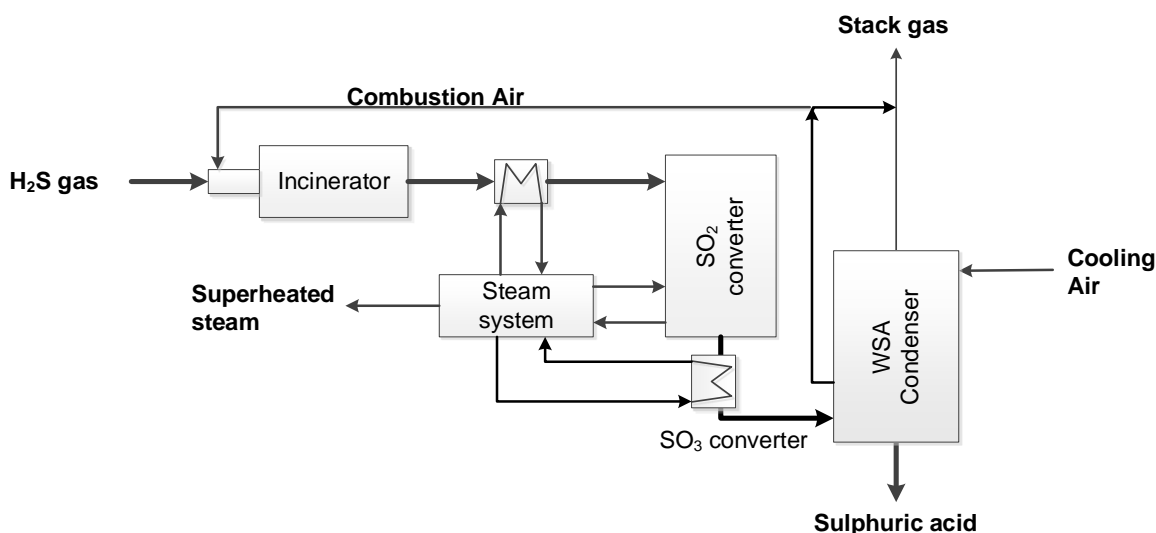
The conventional process for producing H<sub>2</sub>SO<sub>4</sub> uses dry SO<sub>2</sub> gas as raw material. By catalytic oxidation, the SO<sub>2</sub> reacts with the O<sub>2</sub> to form SO<sub>3</sub>, which reacts with H<sub>2</sub>O to generate H<sub>2</sub>SO<sub>4</sub>. This process is well described by King *et al.* (2013). In the conventional H<sub>2</sub>SO<sub>4</sub> process, the feed gas is dried prior to SO<sub>2</sub> oxidation. The company Haldor Topsøe has developed a process called wet gas sulphuric acid (WSA) (Laursen 2007; Sørensen *et al.* 2015), whereby wet SO<sub>2</sub> gas is fed directly into the oxidation step. The SO<sub>2</sub> in the feed gas, which also contains H<sub>2</sub>O<sub>(g)</sub>, O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>, among other chemicals, is oxidized catalytically to form SO<sub>3</sub> (Reaction 2) in a catalytic reactor (SO<sub>2</sub> converter seen in Fig. 2) that contains up to three catalytic beds. The main catalyst reaction is the same as in the conventional process. The reaction is exothermal, so the gas is cooled between the catalytic beds in order to optimize the formation of the SO<sub>3</sub>. After the last catalytic bed, the SO<sub>3</sub> cools and reacts with the H<sub>2</sub>O<sub>(g)</sub> in the feed gas (SO<sub>3</sub> converter seen in Fig. 2) to form H<sub>2</sub>SO<sub>4</sub> in gaseous form (Reaction 3). In the conventional process, the SO<sub>3</sub> is absorbed in liquified H<sub>2</sub>SO<sub>4</sub>. The H<sub>2</sub>SO<sub>4(g)</sub> is then condensed in the WSA condenser to generate strong H<sub>2</sub>SO<sub>4</sub> (Reaction 4). The condensation is carried out at a temperature where very little H<sub>2</sub>O<sub>(g)</sub> condenses, which produces highly concentrated H<sub>2</sub>SO<sub>4</sub>. The WSA condenser is a falling film condenser, with tubes made of acid-resistant boron silicate glass, in which the process gas/ H<sub>2</sub>SO<sub>4</sub> is cooled by air in a cross-current flow. Part of the hot air generated could be used as combustion air in the incinerator (Laursen 2007; King *et al.* 2013). A schematic diagram of the process is shown in Fig. 2.





The heat generated from incineration of the sulphur-containing gases, the SO<sub>2</sub> converter step, and the SO<sub>3</sub> converter step (Reactions 1, 2, and 3), in an industrial application, is used to produce high-pressure (HP) steam. The condensation of the H<sub>2</sub>SO<sub>4</sub> (Reaction 4) is carried out in an air cooler, which generates hot air.

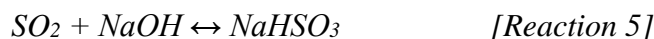
The WSA process is mainly used for feed gases containing H<sub>2</sub>O<sub>(g)</sub> and relatively low amounts of SO<sub>2</sub> (preferably less than 6.5 vol-%). The first WSA plant was installed in 1980 and, by 2012, 110 of such plants were sold throughout the world (King *et al.* 2013). Within the pulp and paper industry, the WSA process is currently offered by Andritz Oy, who have adapted it to kraft pulp mills. Valmet has developed a similar process, also adapted to kraft mills, that produces 50 wt-% to 70 wt-% H<sub>2</sub>SO<sub>4</sub> (Valmet 2017). The first commercial plant of this type was started up in 2017 at the Metsä Bioproduct Mill in Äänekoski, Finland (Valmet 2020). A similar, but smaller, demo plant was also installed at the Smurfit Kappa Piteå mill in Sweden (Valeur *et al.* 2000, 2001).



**Fig. 2.** Schematic diagram of the WSA process

The sulphur-containing gases generated in the reference mill are burned in a dedicated gas burner, which generates SO<sub>2</sub> and CO<sub>2</sub>. The emissions are reduced by chemical absorption in a scrubber, in which NaOH is used as the absorption chemical and reacts with SO<sub>2</sub>, see Reactions 5 and 6. The scrubber liquid generated (mainly NaHSO<sub>3</sub>) is returned to the mill's causticizing plant to maintain the Na/S balance, as seen in Fig. 3. Reaction 5 is favored by lower pH levels, *i.e.* ≤ 8.5 (Schultes 1998), which is advantageous to reduce the amount of NaOH consumed in the scrubber. The scrubber has two-stages, with a pH control at each, which optimize both the absorption of the SO<sub>2</sub> and the consumption of the NaOH. It is assumed that there is not an excessive amount of NaOH added, so no amount of Na<sub>2</sub>SO<sub>3</sub> will be generated according to Reaction 6. Therefore, based on the total consumption of NaOH in the scrubber, the total amount of sulphur in the CNCG generated can be calculated according to Reaction 5. Based on this, the amount of sulphur calculated in the CNCG is approximately 98 kg S/h, which corresponds to 2.4 kg S/ADt. The amount of sulphur released into the CNCG varies between mills, since it depends on the sulphidity and heat treatment in the evaporation and cooking processes. Valmet (2017) estimated the amount of sulphur released into the CNCG to be between 3

kg S/ADt and 7 kg S/ADt. The Smurfit Kappa Piteå, Sweden demo plant released 1.7 kg S/ADt, with the ability to increase it to 4 kg S/ADt by subjecting the black liquor to heat treatment (Valeur *et al.* 2000).



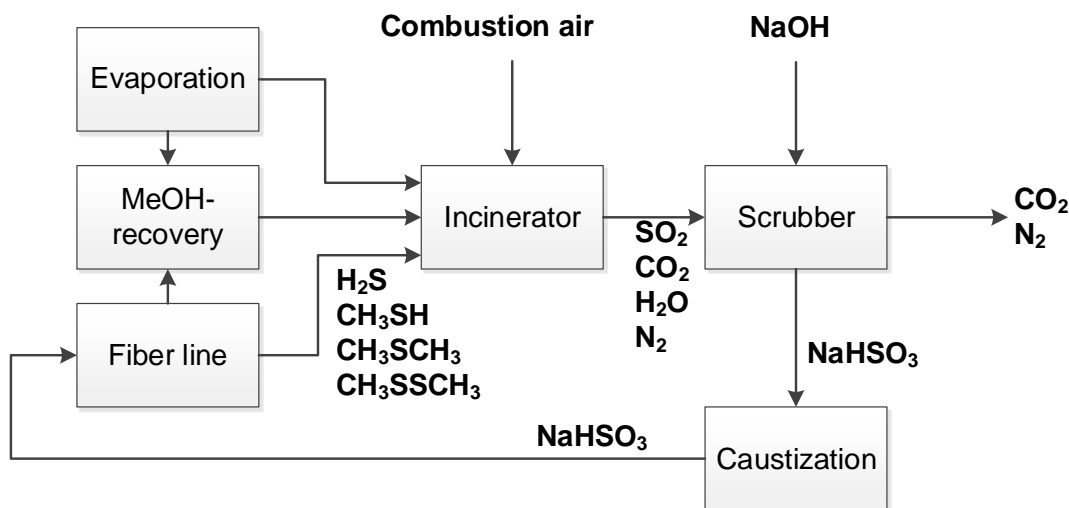
In this study, the calculated amount of sulphur is converted into a typical CNCG composition based on the information obtained from Bordado and Gomes (1998), as can be seen in Table 1.

**Table 1.** Estimated Composition of the Sulphur-Containing Gases

	Flow (kg/h)	Composition (Wt-%)
<b>CNCG</b>	175.4	CH <sub>3</sub> SH: 26.3 CH <sub>3</sub> SCH <sub>3</sub> : 62.3 CH <sub>3</sub> SSCH <sub>3</sub> : 4.0 H <sub>2</sub> S: 4.5 H <sub>2</sub> O: 2.9

In the scenario examined, where H<sub>2</sub>SO<sub>4</sub> is produced rather than scrubbing with NaOH, sulphur from the sulphur-containing gases is recycled within the mill's Na/S balance, as seen in Figs. 3 and 4. The amount of sodium added is reduced since no absorption chemicals are necessary.

The CNCGs generated at the mill have a relatively high H<sub>2</sub>O content, and the resulting flue gas contains a relatively low amount of SO<sub>2</sub>. Therefore, the WSA process is suitable for use, as the wet SO<sub>2</sub> gas can be fed directly to the oxidation step. A process for utilising the sulphur-containing gases in the production of H<sub>2</sub>SO<sub>4</sub> *via* the WSA process was set-up in CHEMCAD, Version 7.1.4 (Houston, TX). CHEMCAD is a flow sheeting software for process modelling that resolves mass- and energy balances as well as chemical and physical equilibrium.



**Fig. 3.** Loop of the current CNCG system

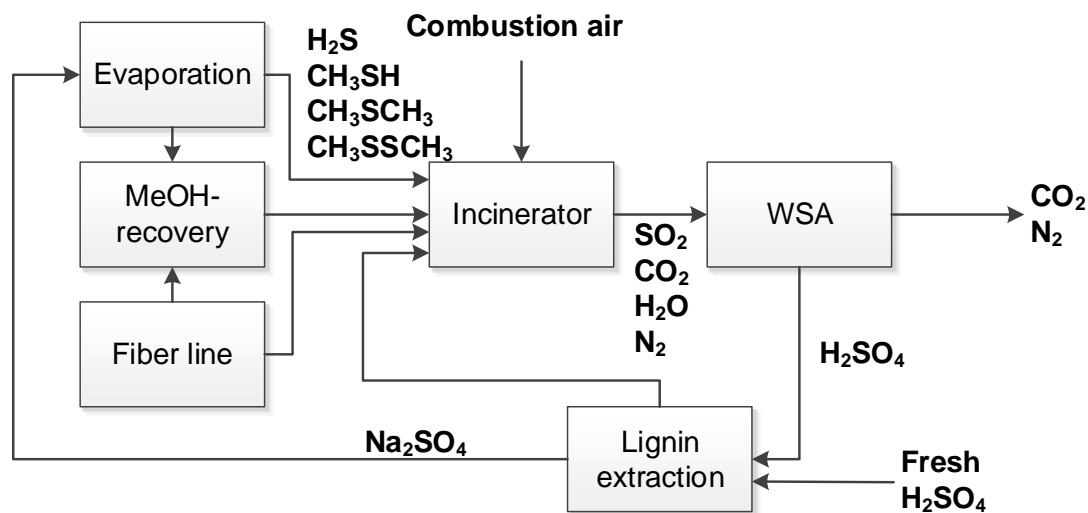


Fig. 4. Loop of a future CNCG system retrofitted for internal production of sulphuric acid

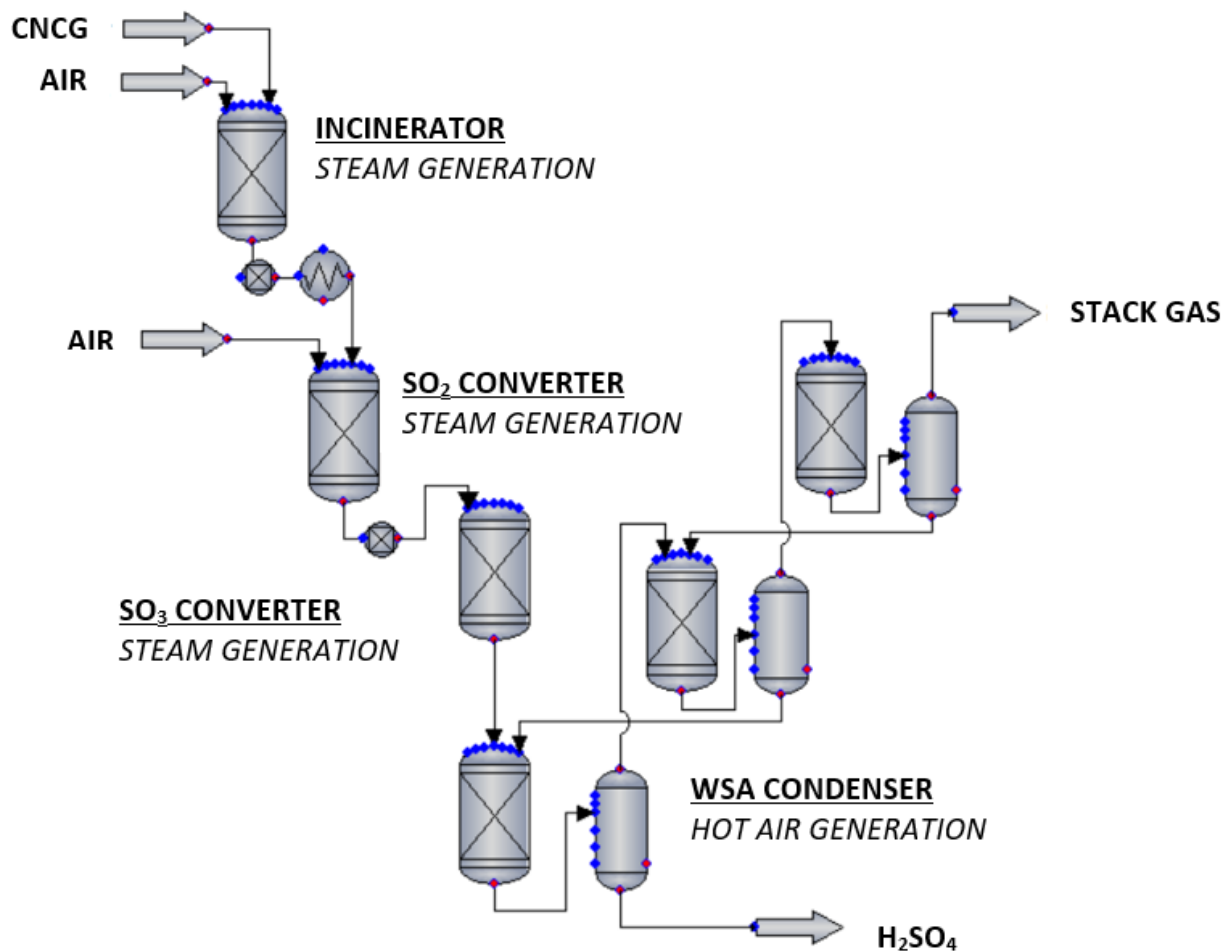


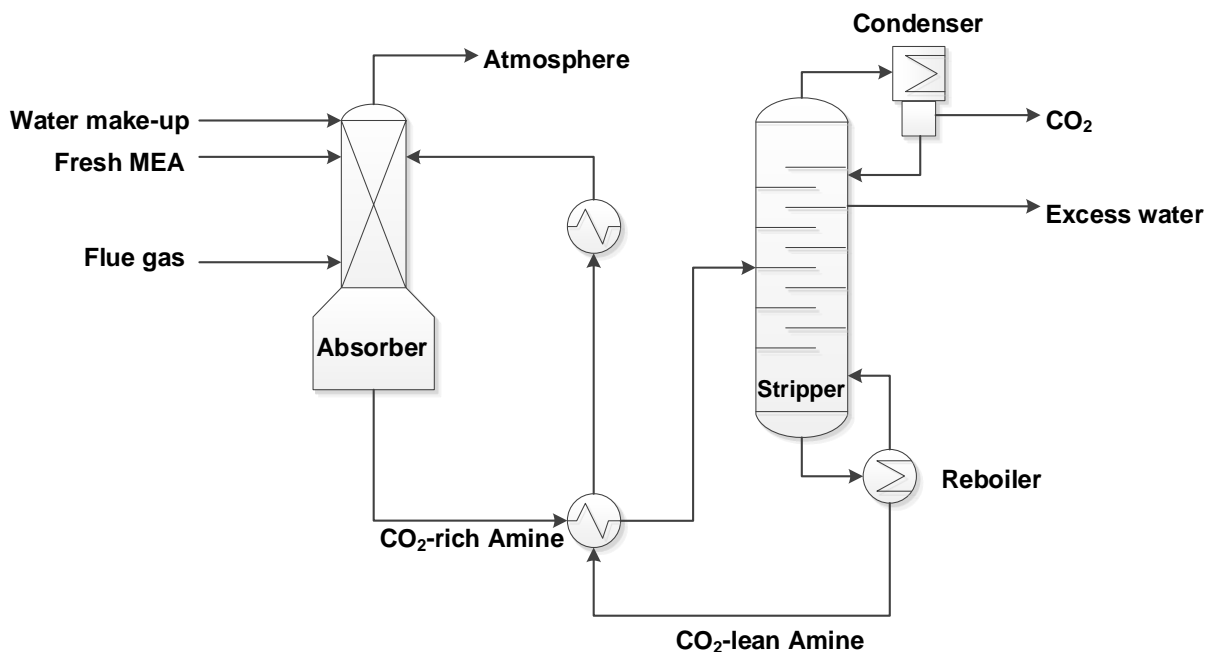
Fig. 5. Schematic diagram of the H<sub>2</sub>SO<sub>4</sub> plant from the CHEMCAD model

The process was simulated with the main input data according to Table 1. The O<sub>2</sub> excess in both the CNCG combustion and the SO<sub>2</sub> converter was set to 1 wt-%. CHEMCAD GIBS (Gibbs Free Energy Reactor) blocks were used for the incineration, SO<sub>2</sub> conversion, SO<sub>3</sub> conversion, and condenser steps. The Gibbs reactor is based on the principal that at chemical equilibrium, the total Gibbs energy of the system has its minimum value. The NTRL was used as the K-value model, and latent heat was used as the enthalpy model. An overview of the CHEMCAD model is shown in Fig. 5.

The model was validated by comparing the equilibrium constants calculated for Reactions 2 and 3 to data available in the literature (Kjelstrup and Island 1999; King *et al.* 2013). The model validation shows reasonably consistent values, indicating that the gas composition from the simulation model shows good compliance with data from literature.

## CO<sub>2</sub> Capture

The post-combustion method refers to the capture of CO<sub>2</sub> from flue gases generated *via* the combustion of fossil fuels or biomass in air. Rather than releasing flue gases directly into the atmosphere, CO<sub>2</sub> is separated, and the remaining CO<sub>2</sub>-lean flue gas is discharged instead (Metz *et al.* 2005). Chemical absorption is the most common method to capture CO<sub>2</sub> and it is one of a few techniques that are practical for removing large amounts of CO<sub>2</sub>. Compared to other post-combustion processes, chemical absorption ensures high absorption efficiency and selectivity while using a relatively low amount of energy (Metz *et al.* 2005; Akanksha *et al.* 2007; Cormos *et al.* 2009; Rochelle 2009).



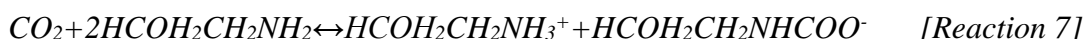
**Fig. 6.** Schematic diagram of CO<sub>2</sub> capture *via* chemical absorption

Chemical absorption is suitable to recover CO<sub>2</sub> from flue gases due to its low concentration of CO<sub>2</sub>. This process does not require design modifications to the boiler. There are several different alkanolamines that are used as absorbents in commercial use, such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), triethanolamine (TEA), diisopropanolamine (DIPA), and diglycolamine (DGA). MEA is a well-known and used chemical for chemical absorption and thus used in this



work. Prior to the capture of CO<sub>2</sub>, the flue gas normally requires cooling and treatment to reduce the number of particulates and other impurities that may be present. Allowing flue gas to encounter an absorbent in an absorber column enables the CO<sub>2</sub> to be captured. The absorbent loaded with CO<sub>2</sub> is then transported to a stripper, where it is heated to release the CO<sub>2</sub> and regenerate the absorbent. The regenerated absorbent is then recycled for further CO<sub>2</sub> capture (Chakravarti *et al.* 2001; Metz *et al.* 2005; Edwards 2009), as can be seen in Fig. 6.

The overall reaction between the CO<sub>2</sub> and the MEA is shown in Reaction 7. The reaction involves a weak base (MEA) and a weak acid (CO<sub>2</sub>). The equilibrium occurs in the liquid phase, where the CO<sub>2</sub> is absorbed in the aqueous solution of the MEA (Akanksha *et al.* 2007; Cormos *et al.* 2009).



Proven chemical absorption processes are commercially available today. Existing production plants have a production capacity that vary between 6 tCO<sub>2</sub>/day and 800 tCO<sub>2</sub>/day (Metz *et al.* 2005).

The potential amount of CO<sub>2</sub> available in a kraft pulp mill well exceeds the amount required in the lignin extraction process. Although the recovery boiler generates the largest quantities of flue gas and CO<sub>2</sub>, it has a lower fraction of CO<sub>2</sub> compared to the flue gas that exits the lime kiln. The CNCG boiler generates a relatively small amount of flue gas. Therefore, the flue gas from the lime kiln is the most appropriate source of CO<sub>2</sub> for this application because it has a reasonable amount of CO<sub>2</sub> at a relatively high concentration. Flue gas with a higher concentration of CO<sub>2</sub> causes a lower specific steam consumption (Freguia and Rochelle 2003; Garðarsdóttir *et al.* 2018).

The flow and composition of the flue gas from the lime kiln were calculated based on the amount of tall oil pitch that was consumed as fuel in the lime kiln and the CO<sub>2</sub> that was generated during the calcining process. The conversion of calcium carbonate (CaCO<sub>3</sub>) into calcium oxide (CaO) in the lime kiln can be seen in Reaction 8.



The composition of the flue gas from the lime kiln was calculated and is reported in Table 2. Approximately 20% and 80% of the CO<sub>2</sub> generated was from the lime kiln fuel and the calcining process, respectively. In theory, the total amount of CO<sub>2</sub> available in the lime kiln flue gas should exceed the amount of CO<sub>2</sub> required for the extraction of 45,000 tons of lignin per year by a factor of approximately 30 (Kihlman 2016).

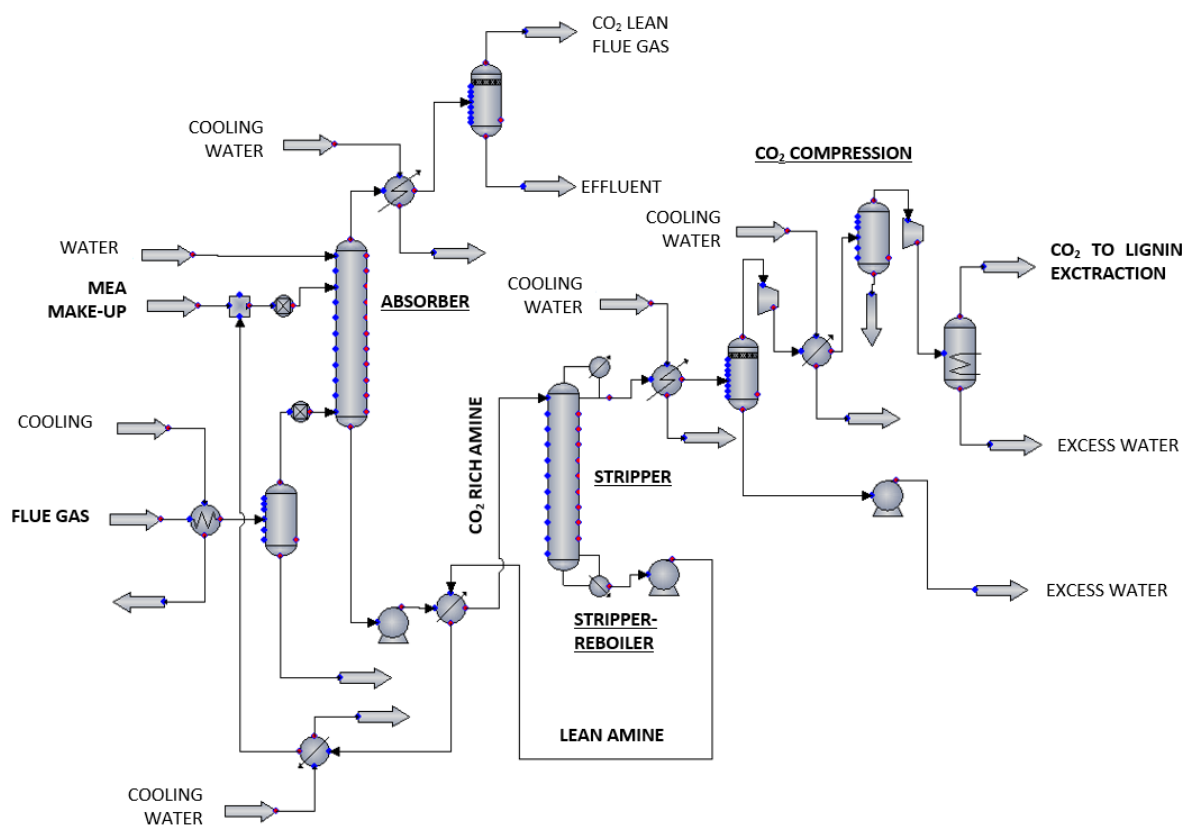
**Table 2.** Calculated Composition of the Flue Gas from the Lime Kiln

Source	Flow (kg/h)	Composition (Wt-%)
Lime Kiln	84 124	CO <sub>2</sub> : 31.6 SO <sub>2</sub> : 0.0 N <sub>2</sub> : 41.7 O <sub>2</sub> : 5.6 H <sub>2</sub> O: 21.1

Chemical absorption using MEA as the absorbent is an appropriate method to recover CO<sub>2</sub> from flue gases, so it was chosen for the CO<sub>2</sub> capture at the reference mill. A simulation model in CHEMCAD was established to investigate the impact of a chemical absorption process related to the pulp mill. The input data, along with the variables in the simulation model, are compiled in Table 3. The CHEMCAD block and Simultaneous Correction Distillation System (SCDS) were used for the absorber and the stripper. The Amine Model, a built-in package in CHEMCAD, was used for the thermodynamic calculations. The Amine Model uses the Kent-Eisenberg method, which is a simplified way of modelling reactions in a gas sweetening system. An overview of the CHEMCAD model is shown in Fig. 7.

**Table 3.** Input Data and Variables Used in the Chemical Absorption Process Using MEA as the Solvent

Input	Value	Unit
Flue Gas Temperature	250	°C
Flue Gas Temperature Absorber Inlet	50	°C
Solvent (MEA) Concentration	30	%
Pressure Top Absorption Column	1	Bar (abs)
Number of Absorption Column Stages	12	stages
Number of Stripper Stages	15	stages
Temperature the Inlet Stripper	105	°C
Pressure of the Top Stripper	1.7	Bar (abs)
CO <sub>2</sub> Final Pressure	15	Bar (abs)



**Fig. 7.** Schematic diagram of the CO<sub>2</sub> capture plant from the CHEMCAD model

## RESULTS AND DISCUSSION

The combustion of the CNCG flow generated a flue gas that contained approximately 5 vol-% SO<sub>2</sub>, 13 vol-% H<sub>2</sub>O, 7 vol-% CO<sub>2</sub>, 1 vol-% O<sub>2</sub>, and 74 vol-% N<sub>2</sub>. The SO<sub>2</sub> content of the flue gas was within the preferred limits for the WSA process. The H<sub>2</sub>SO<sub>4</sub> simulation model was optimized to produce as much H<sub>2</sub>SO<sub>4</sub> as possible. The results and detailed input data are presented in Table 4, which is based on the overall input data in Table 1 and the process characteristics, as illustrated in Figs. 8, 9, 10, and 11.

The gas flows of SO<sub>2</sub>, SO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> were calculated based on the theoretical equilibrium conditions, and the results are plotted in Fig. 8 as a function of the temperature in the incinerator. Figure 8 shows that a low amount of SO<sub>2</sub> is generated at lower temperatures, and the SO<sub>2</sub> production reached a maximum at approximately 1,000 °C. This temperature will also achieve a good burn-out of all the combustibles in the incinerator (Wallenius 2020).

**Table 4.** Input Values Used in the H<sub>2</sub>SO<sub>4</sub> WSA-Process Simulation Model and the Results Obtained

Input	Value	Unit	Comments
Temperature Incinerator	950	°C	Value chosen to obtain high yield of SO <sub>2</sub> and keep the incineration temperature at a desired level, see Fig. 8.
Temperature SO <sub>2</sub> Converter	430	°C	Value chosen to obtain maximum formation of SO <sub>3</sub> , see Fig. 9.
Temperature SO <sub>3</sub> Converter	270	°C	
Temperature WSA Condenser, Top	100	°C	Value chosen to minimize the escape of the H <sub>2</sub> SO <sub>4</sub> (g) into the stack gas, see Fig. 11.
Pressure WSA Condenser, Bottom	1.1	Bar (abs)	
Pressure WSA Condenser, Bottom	1.05	Bar (abs)	
Results	Value	Unit	Comments
Temperature WSA Condenser, Bottom	243	°C	
Produced H <sub>2</sub> SO <sub>4</sub> (as 100 wt-%)	304	kg/h	Based on input according to the above and Table 1.
Conc. H <sub>2</sub> SO <sub>4</sub>	94	Wt-%	Based on input according to the above and Table 1.
Total Cooling Demand	1.5	MW	Total amount of heat generated during the process, some of which is normally used to produce steam (see below).
Generated Heat Available to Produce HP-steam	1.25	MW	Heat generated during incineration and in the SO <sub>2</sub> and SO <sub>3</sub> converters.

The catalytic oxidation of the SO<sub>2</sub> to SO<sub>3</sub> is exothermic, so the catalytic beds in the SO<sub>2</sub> converter are cooled to optimize the formation of SO<sub>3</sub>. The maximum formation was reached at a temperature of approximately 430 °C, as shown in Fig. 9. However, the total amount of the H<sub>2</sub>SO<sub>4</sub> produced in the WSA process did not change until the temperature reached 560 °C. This indicates that the remaining SO<sub>2</sub> was converted into SO<sub>3</sub> and, eventually, H<sub>2</sub>SO<sub>4</sub> later in the process.

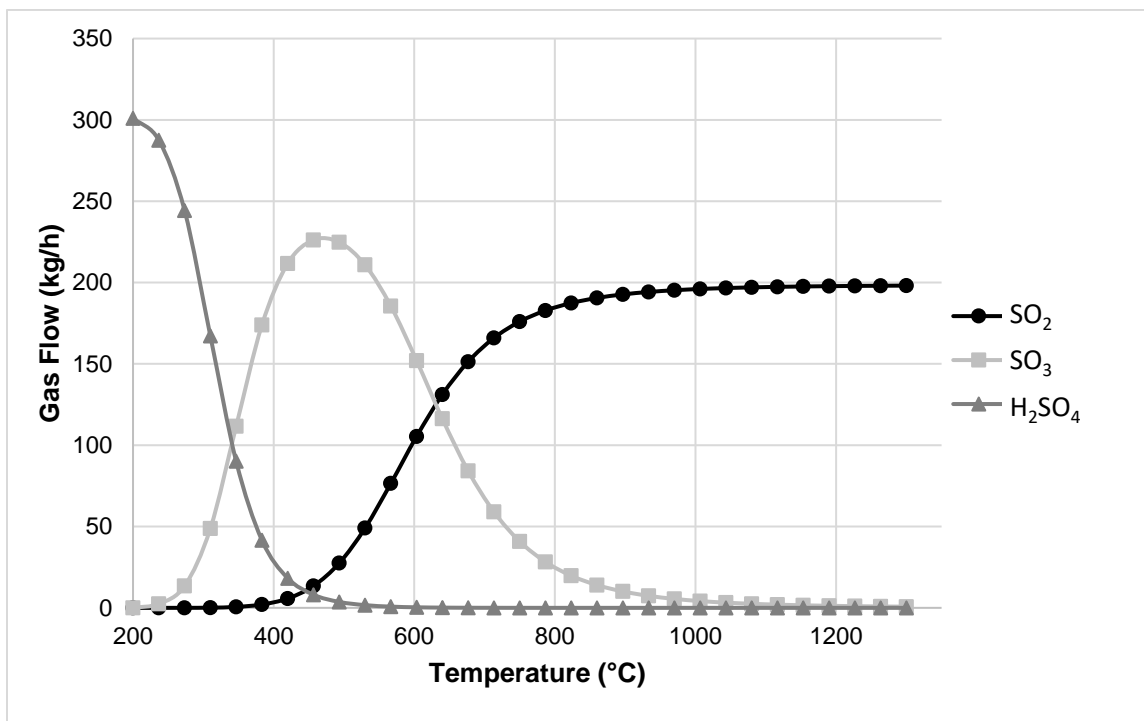


Fig. 8. Gas flow based on the theoretical equilibrium conditions at different temperatures in the GIBS incinerator block

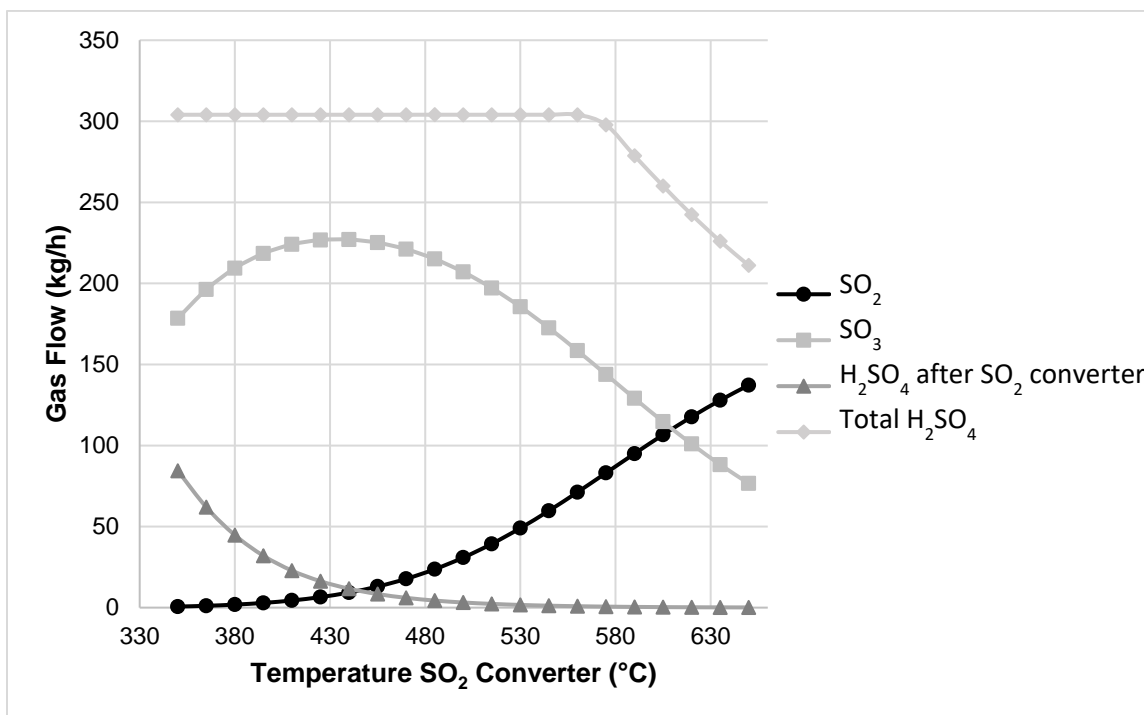
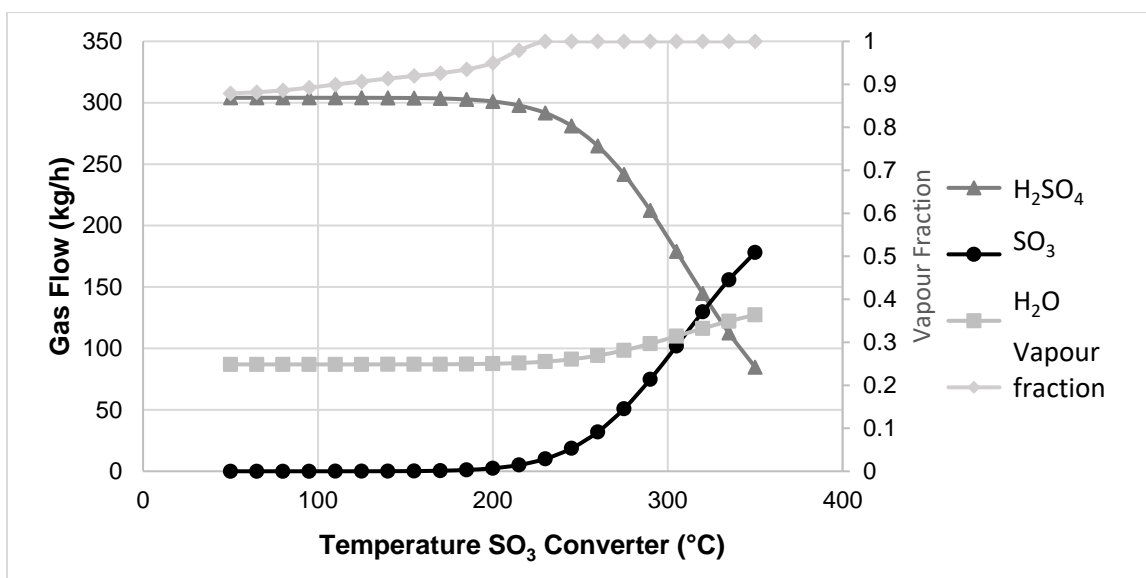


Fig. 9. The quantities of SO<sub>2</sub>, SO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> generated in the SO<sub>2</sub> converter at different temperatures. The total amount of H<sub>2</sub>SO<sub>4</sub> produced in the WSA process is also shown.

The SO<sub>3</sub> is hydrated into H<sub>2</sub>SO<sub>4(g)</sub> in the SO<sub>3</sub> converter, according to Reaction 3. Although this reaction is promoted by a low temperature (King *et al.* 2013), as seen in Fig. 10, corrosion issues dictate the importance of the H<sub>2</sub>SO<sub>4</sub> being kept in gaseous form before entering the WSA condenser. The acid dew point, which depends on the concentrations of

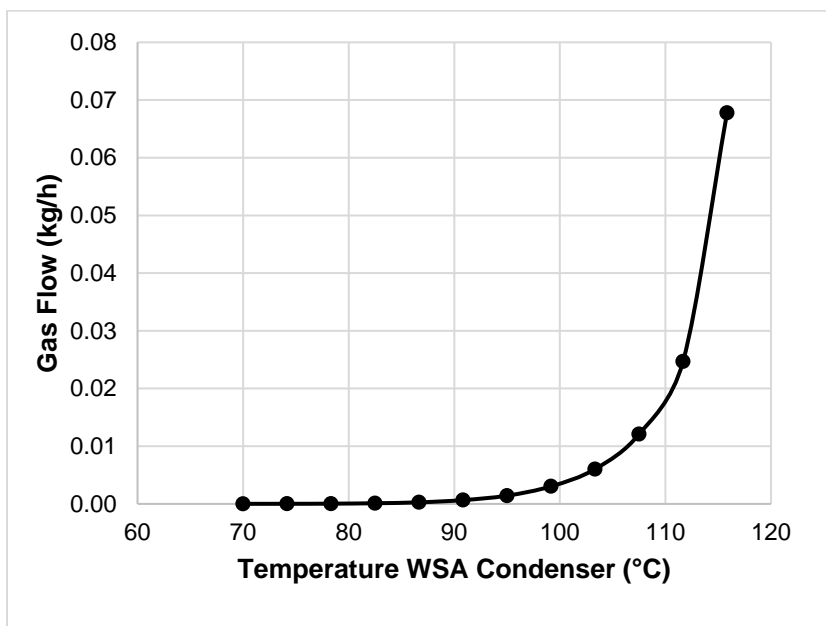
the  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  in the gas, is typically between 220 °C to 265 °C (King *et al.* 2013). Figure 10 shows that the maximum yield of the  $\text{H}_2\text{SO}_4$  after the  $\text{SO}_3$  converter, without any condensation, is achieved at a temperature of approximately 230 °C. The literature reports the normal operating temperature in this  $\text{SO}_3$  converter stage to be 250 °C to 290 °C (King *et al.* 2013; Sørensen *et al.* 2015). This operating temperature facilitates the energy from the hydration to be available at a higher temperature level, but it also provides a margin that hinders the condensation of the  $\text{H}_2\text{SO}_4$  and potential corrosion problems. The  $\text{SO}_3$  that remains after the  $\text{SO}_3$  converter is hydrated in the WSA condenser to produce  $\text{H}_2\text{SO}_4$ .



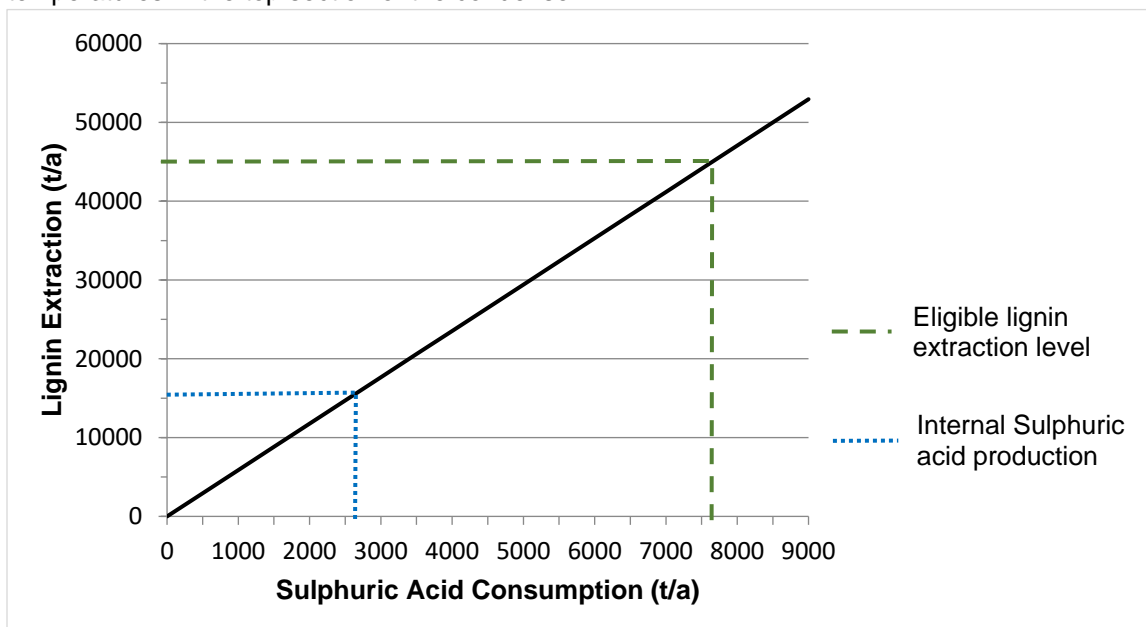
**Fig. 10.** The amount of the  $\text{H}_2\text{SO}_4$  generated in the  $\text{SO}_3$  converter at different temperatures. The vapor fraction and the amounts of the  $\text{H}_2\text{O}$  and the  $\text{SO}_3$  exiting the  $\text{SO}_3$  converter are also shown.

After it is processed in the  $\text{SO}_3$  converter, the process gas is cooled further in the WSA condenser, which hydrates the remaining  $\text{SO}_3$  and condenses the  $\text{H}_2\text{SO}_4$ . The WSA condenser is a counter-current heat exchanger in which the bottom temperature was found to be approximately 243 °C at the assumed pressure, which produces  $\text{H}_2\text{SO}_4$  with a high level of consistency. The temperature in the upper section was set to 100 °C to minimize the escape of the  $\text{H}_2\text{SO}_{4(g)}$  into the stack gas (Fig. 11).

Based on the calculated CNCG flow and the optimized input data, 2,600 tons of  $\text{H}_2\text{SO}_4$  can be produced annually, as seen in Table 4. A lignin extraction rate of 45,000 tons per annum (TPA) means that the  $\text{H}_2\text{SO}_4$  that is produced should cover 32% of the amount required (Kihlman 2016). As can be seen in Fig. 12, the amount of  $\text{H}_2\text{SO}_4$  that is produced corresponds to a lignin extraction rate of 15,250 TPA. Even if the amount of  $\text{H}_2\text{SO}_4$  produced is insufficient for the desired lignin extraction rate, it can be very important for the mill's Na/S balance. The amount of fresh  $\text{H}_2\text{SO}_4$  required will be greatly reduced, which will also reduce the higher removal rate of the ESP ash, and thereby maintain the Na/S balance. As described by Kihlman (2016), the lignin extraction will have a large impact on the removal of the ESP ash. The annual economic value of the  $\text{H}_2\text{SO}_4$  produced is approximately 180,000€. However, the total economic value is much higher considering that less NaOH make-up chemical is required, compared to the addition of only fresh  $\text{H}_2\text{SO}_4$ . Compared to  $\text{H}_2\text{SO}_4$ , NaOH is a much more expensive chemical, at approximately 9× the cost compared to  $\text{H}_2\text{SO}_4$ .



**Fig. 11.** The mass flow of the  $\text{H}_2\text{SO}_4$  in the stack gas exiting the WSA condenser at different temperatures in the top section of the condenser



**Fig. 12.** The consumption of  $\text{H}_2\text{SO}_4$  at the different lignin extraction rates

Figure 12 illustrates the fact that the  $\text{H}_2\text{SO}_4$  that is produced will only cover a limited lignin extraction rate (Lake *et al.* 2015; Kihlman 2016). There are nevertheless various potential methods and processes available that can increase the amount of sulphur-containing gases available in a kraft pulp mill for the production of  $\text{H}_2\text{SO}_4$ , such as steam-stripping (Nilsson 2017), black liquor oxidation, heat treatment, and the acidification of green liquor (Valeur *et al.* 2000; Välimäki *et al.* 2015; Valmet 2017). Acidifying green liquor by stripping it with  $\text{CO}_2$  is probably the most effective way to increase the internal production of  $\text{H}_2\text{SO}_4$ .

The capture of CO<sub>2</sub> *via* chemical absorption consumes a relatively high amount of energy in order to regenerate the absorbent. Unlike most studies of carbon capture and storage (CCS), there are no incentives in this case to capture as much CO<sub>2</sub> as possible because the amount of CO<sub>2</sub> available in the flue gas greatly exceeds the demand for lignin extraction. Therefore, it was investigated whether there are energy benefits to be gained by running the process at a lower yield. Figures 13 and 14 show that at high CO<sub>2</sub> yields, the energy consumption is expected to be very high, but the energy consumption decreases as the CO<sub>2</sub> yield decreases. However, the energy consumption levels out at a CO<sub>2</sub> yield of approximately 85%, so it is unrealistic to attain a lower CO<sub>2</sub> yield. Therefore, a reasonable CO<sub>2</sub> yield should be approximately 85%, which would ensure that the energy consumption remains at a low level and keep the equipment dimensioning flow of the flue gases at a reasonable level.

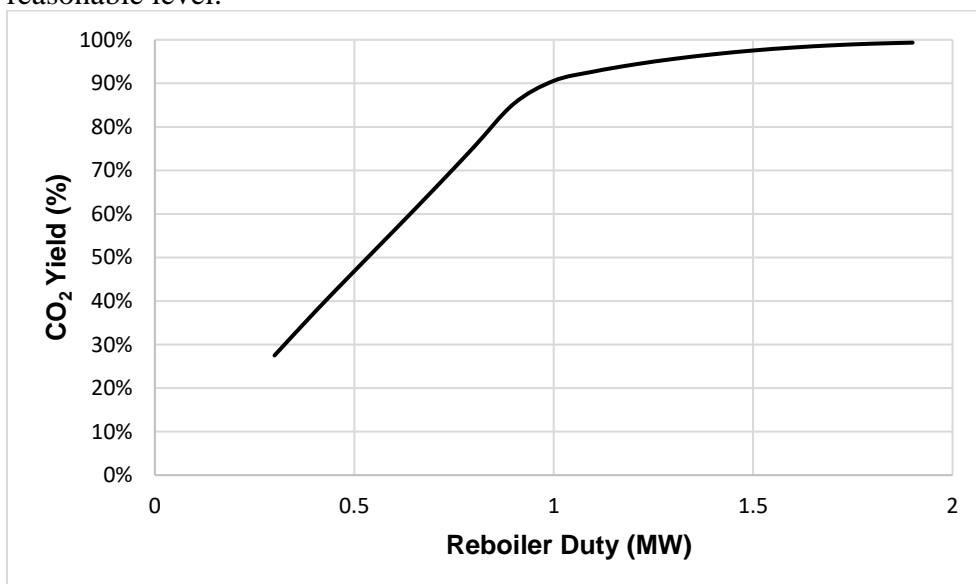


Fig. 13. The CO<sub>2</sub> yield versus the stripper reboiler duty

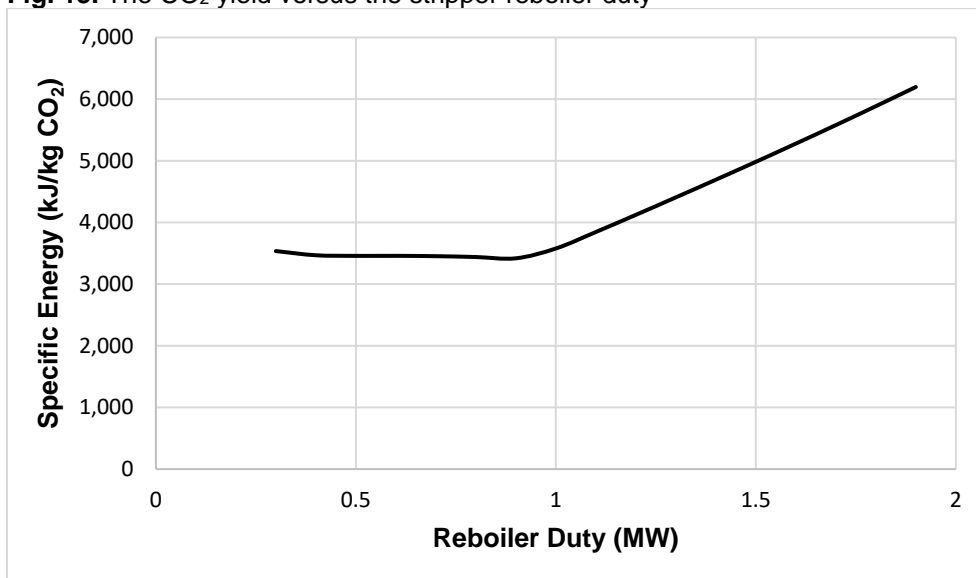


Fig. 14. The energy consumption per kg captured CO<sub>2</sub> versus stripper reboiler duty

The energy consumption at a CO<sub>2</sub> yield of 85% is 3,420 kJ/kg CO<sub>2</sub>, as can be seen in Table 5. The CO<sub>2</sub> consumption for the lignin extraction is approximately 0.15 to 0.25

per ton of lignin (Kihlman 2016). Therefore, the annual consumption of CO<sub>2</sub> at a lignin extraction rate of 45,000 TPA is approximately 8,100 tons. The capture of this CO<sub>2</sub> corresponds to an annual energy consumption of 8 GWh. The relatively small amount of captured CO<sub>2</sub> means that the energy consumption necessary will only have a minor impact on the mill's energy balance in terms of both heat and electricity. A lignin extraction rate of 45,000 TPA will decrease the quantity of fuel (*i.e.* the amount of lignin in the black liquor) fed into the recovery boiler by approximately 335 GWh per year, which will generate significantly less steam.

The chemical absorption process requires low pressure (LP) steam to regenerate the absorbent, cooling water for the condensers, flue gas, amine cooling, and electricity for pumping and CO<sub>2</sub> compression (Table 5).

**Table 5.** Utility Consumption per kg of Captured CO<sub>2</sub> (at a capture rate of 85%)

Utility	Value	Unit	Comments
LP-steam	3,420	kJ/kg CO <sub>2</sub>	
Cooling Water	5,840	kJ/kg CO <sub>2</sub>	Heat integration regarding lean and rich MEA solvent has been considered; CO <sub>2</sub> -lean flue gas cooled to 50 °C.
Electricity	213	kJ/kg CO <sub>2</sub>	Pumping and compression of CO <sub>2</sub> to 15 bar (abs).

Based on a CO<sub>2</sub> yield of 85%, the maximum amount of CO<sub>2</sub> captured from the lime kiln flue gas is approximately 190,000 TPA, which well exceeds the requirement for lignin extraction. There are other possible applications for CO<sub>2</sub> at such a mill, but the potential for using other methods that are currently available is relatively low. Kuparinen *et al.* (2019) described how CO<sub>2</sub> can be used for acidulation in the production of tall oil and to produce precipitated calcium carbonate. The acidulation of raw soap, which is used to produce tall oil, is normally performed by adding H<sub>2</sub>SO<sub>4</sub>. Sometimes, spent acid from the chlorine dioxide plant can also be added. However, CO<sub>2</sub> is a weaker acid than H<sub>2</sub>SO<sub>4</sub> and only some of the H<sub>2</sub>SO<sub>4</sub> that is required can be replaced with CO<sub>2</sub>, which corresponds to 4 to 6 kg CO<sub>2</sub>/ADt (Kuparinen *et al.* 2019). Although the production of CaCO<sub>3</sub> varies depending on the local demand, the consumption of CO<sub>2</sub> can be 20 kg CO<sub>2</sub>/ADt (Kuparinen *et al.* 2019). These alternative applications and uses for CO<sub>2</sub>, combined with lignin extraction methods, can consume up to 17,200 TPA of CO<sub>2</sub>. This is a small volume of the total amount of CO<sub>2</sub> available of the flue gas generated in the lime kiln, but nevertheless a step in the right direction to capture and utilize CO<sub>2</sub>.

## CONCLUSIONS

1. The internal production of H<sub>2</sub>SO<sub>4</sub> is an effective way to close a kraft pulp mill chemical loop and reduce emissions. The potential production of H<sub>2</sub>SO<sub>4</sub> from existing sulphur-containing gases at the mill that was studied is sufficient for lignin extraction rate of 15,250 TPA, which is slightly less than the volume of existing full-scale industrial plants. Utilizing existing process streams to produce H<sub>2</sub>SO<sub>4</sub> and moving towards a more circular approach may be crucial to implement a lignin extraction process. All efforts that are made to minimize the impact on the mill's balance will be beneficial.



2. The total amount of CO<sub>2</sub> available at such a mill well exceeds the requirements of lignin extraction. Chemical absorption is an energy-intensive process. Compared to the mill's total energy balance, the energy required to capture the amount of CO<sub>2</sub> necessary for the lignin extraction process is minor. This also applies to other utilities that are required, such as cooling water.
3. In this study, only a small amount of the total CO<sub>2</sub> present in the flue gas generated in the lime kiln was captured. As interest in bioenergy carbon capture and storage (BECCS) grows, CO<sub>2</sub> can be utilized for lignin extraction. In combination with lignin extraction, BECCS will increase the mill's consumption of steam significantly. The mill's capacity to produce steam will be a limiting factor in capturing the large amount of CO<sub>2</sub> present in the flue gas unless investments are made. Therefore, it may be relevant to design a BECCS system to capture a limited amount of CO<sub>2</sub> so that the mill's energy balance can be fulfilled without making extensive changes and/or investing in auxiliary equipment.
4. Applying this circular approach to lignin extraction is an innovative process. It could be vital, both environmentally and economically, for the future development and expansion of the kraft lignin market.
5. For further studies it would be of interest to examine the possibilities to increase the amount of sulphur-containing gases and thereby enabling even higher production of sulphuric acid. One wants to find out which methods would be most suitable, how much sulphuric would be possible to produce, and in what way would this affect the mill's Na/S balance.

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## REFERENCES CITED

- Akanksha, Pant, K. K., and Srivastava, V. K. (2007). "Carbon dioxide absorption into monoethanolamine in a continuous film contactor," *Chemical Engineering Journal* 133(1-3). DOI: 10.1016/j.cej.2007.02.001
- Andersson, K. (2019). "Stor potential för att fånga in och lagra bio-CO<sub>2</sub>," *Bioenergy* (2).
- Benali, M., Périn-Levasseur, Z., Savulescu, L., Kouisni, L., Jemaa, N., Kudra, T., and Paleologou, M. (2014). "Implementation of lignin-based biorefinery into a Canadian softwood kraft pulp mill: Optimal resources integration and economic viability assessment," *Biomass and Bioenergy* 67, 473-482. DOI: 10.1016/j.biombioe.2013.08.022

- Bordado, J. C. M., and Gomes, J. F. P. (1998). "Characterisation of non-condensable sulphur containing gases from kraft pulp mills," *Chemosphere* 37(7), 1235-1240. DOI: 10.1016/S0045-6535(98)00121-0
- Chakravarti, S. K., Gupta, A., and Hunek, B. (2001). "Advanced technology for the capture of carbon dioxide from flue gases," in: *First National Conference on Carbon Sequestration*, Washington, DC.
- Cormos, A.-M., Gaspar, J., and Padurean, A. M. (2009). "Modeling and simulation of carbon dioxide absorption in monoethanolamine in packed absorption columns," *Studia Universitatis Babeş-Bolyai, Chemia* (3).
- Dessbesell, L., Paleologou, M., Leitch, M., Pulkki, R., and Xu, C. (2020). "Global lignin supply overview and kraft lignin potential as an alternative for petroleum-based polymers," *Renewable and Sustainable Energy Reviews* 123, article no. 109768. DOI: 10.1016/j.rser.2020.109768
- Edwards, J. E. (2009). *Power Plant Carbon Capture with CHEMCAD*, Chemstations, Houston, TX.
- Frederick, W. J., Danko, J. P., and Ayers, R. J. (1996). "Controlling TRS emissions from dissolving-tank vent stacks," *TAPPI Journal* 79(6), 144-148.
- Freguia, S., and Rochelle, G. T. (2003). "Modeling of CO<sub>2</sub> capture by aqueous monoethanolamine," *AIChE Journal* 49(7), 1676-1686. DOI: 10.1002/aic.690490708
- Garðarsdóttir, S. O., Normann, F., Skagestad, R., Johnsson, F. (2018). "Investment costs and CO<sub>2</sub> reduction potential of carbon capture from industrial plants - A Swedish case study," *International Journal of Greenhouse Gas Control* 76, 111-124. DOI: 10.1016/j.ijggc.2018.06.022
- Goheen, D. W. (1964). "Chemistry of some sulfur compounds derived from lignin," *TAPPI Journal* 47(6), 14A.
- Hamaguchi, M., Vakkilainen, E. K., and Ryder, P. L. (2011). "The impact of lignin removal on the dimensioning of eucalyptus pulp mills," *Appita Journal* 64(5), 433-439.
- Hektor, E., and Berntsson, T. (2007). "Future CO<sub>2</sub> removal from pulp mills - Process integration consequences," *Energy Conversion and Management* 48(11), 3025-3033. DOI: 10.1016/j.enconman.2007.06.043
- Hektor, E., and Berntsson, T. (2009). "Reduction of greenhouse gases in integrated pulp and paper mills: Possibilities for CO<sub>2</sub> capture and storage," *Clean Technologies and Environmental Policy* 11(1), 59-65. DOI: 10.1007/s10098-008-0166-3
- Hubbe, M., Alén, R., Paleologou, M., Kannangara, M., and Kihlman, J. (2019). "Lignin recovery from spent alkaline pulping liquors using acidification, membrane separation, and related processing steps: A Review" *BioResources* 14(1), 2300-2351. DOI: 10.15376/biores.14.1.2300-2351
- Järvensivu, M., Mäenpää, T., Jämsä-Jounela, S.-L., and Saari, K. (2000). "Field survey of reduced-sulfur emissions from a modern Finnish pulp mill," *Environmental Progress*, 19(3), 147-156.
- Jönsson, J., and Berntsson, T. (2012). "Analysing the potential for implementation of CCS within the European pulp and paper industry," *Energy* 44(1), 641-648. DOI: 10.1016/j.energy.2012.05.028
- Kalatjari, H. R., Haghtalab, A., Nasr, M. R. J., and Heydarinasab, A. (2019). "Experimental, simulation and thermodynamic modeling of an acid gas removal pilot plant for CO<sub>2</sub> capturing by mono-ethanol amine solution," *Journal of Natural Gas Science and Engineering* 72, article no. 103001. DOI: 10.1016/j.jngse.2019.103001

- Kannangara, M., Marinova, M., Fradette, L., and Paris, J. (2012). "Lignin recovery by acid precipitation in a kraft mill: An energy perspective," *Journal of Science & Technology for Forest Products and Processes* 2(4), 28-32.
- Kihlman, J. (2016). "The sequential liquid-lignin recovery and purification process: Analysis of integration aspects for a kraft pulp mill," *Nordic Pulp & Paper Research Journal* 31(4), 573-582. DOI: 10.3183/npprj-2016-31-04-p573-582
- King, M. J., Davenport, W. G., and Moats, M. S. (2013). *Sulfuric Acid Manufacture: Analysis, Control and Optimization*, Elsevier, Amsterdam, Netherlands.
- Kjelstrup, S., and Island, T. V. (1999). "The driving force distribution for minimum lost work in a chemical reactor far from equilibrium: Oxidation of SO<sub>2</sub>," *Computers & Chemical Engineering* 23(1), 5987-5990. DOI: 10.1016/S0098-1354(99)80233-6
- Kuparinen, K., Vakkilainen, E., and Tynjälä, T. (2019). "Biomass-based carbon capture and utilization in kraft pulp mills," *Mitigation and Adaption Strategies for Global Change* 24(7), 1213-1230. DOI: 10.1007/s11027-018-9833-9
- Lake, M. A., Blackburn, J. C., and Stevens, D. (2015). "SLRP mass balance interface streams," <http://www.liquidlignin.com>.
- Laursen, J. K. (2007). "Details advances in sulphur recovery by the WSA process," <https://www.hydrocarbonengineering.com>.
- McKean, W. T., Hrutfiord, B. F., and Sarkanen, K. V. (1965). "Kinetic analysis of odor formation in the kraft pulping process," *TAPPI Journal* 48(12), 699-704.
- Metsä Fibre. (2020). "Metsä Fibre," <https://www.metsafibre.com>.
- Metz, B., Ogunlade, D., de Coninck, H., Loos, M., and Meyer, L. (2005). *IPCC Special Report on Carbon Dioxide Capture and Storage*, IPCC, Cambridge, England.
- Möllersten, K., Gao, L., Yan, J., and Obersteiner, M. (2004). "Efficient energy systems with CO<sub>2</sub> capture and storage from renewable biomass in pulp and paper mills," *Renewable Energy* 29(9), 1583-1598. DOI: 10.1016/j.renene.2004.01.003
- Möllersten, K., Yan, J., and Westermark, M. (2003). "Potential and cost-effectiveness of CO<sub>2</sub> reductions through energy measures in Swedish pulp and paper mills," *Energy* 28(7), 691-720. DOI: 10.1016/S0360-5442(03)00002-1
- Nilsson, K. (2017). *Raising the Efficiency of Black Liquor Lignin Extraction*, Master's Thesis, Department of Chemical Engineering, Lund University, Lund, Sweden.
- Norgren, M., and Edlund, H. (2014). "Lignin: Recent advances and emerging applications," *Current Opinion in Colloid & Interface Science* 19(5), 409-416. DOI: 10.1016/j.cocis.2014.08.004
- Onarheim, K., Santos, S., Kangas, P., and Hankalin, V. (2017). "Performance and costs of CCS in the pulp and paper industry part 1: Performance of amine-based post-combustion CO<sub>2</sub> capture," *International Journal of Greenhouse Gas Control* 59, 58-73. DOI: 10.1016/j.ijggc.2017.02.008
- Périn-Levasseur, Z., Savulescu, L., and Benali, M. (2011). "Lignin production path assessment: Energy, water, and chemical integration perspective," *Journal of Science & Technology for Forest Products and Processes* 1(3), 25-30.
- Rochelle, G. T. (2009). "Amine scrubbing for CO<sub>2</sub> capture," *Science* 325(5498), 1652-1654. DOI: 10.1126/science.1176731
- Schultes, M. (1998). "Absorption of sulphur dioxide with sodium hydroxide solution in packed columns," *Chemical Engineering & Technology* 21(2), 201-209. DOI: 0930-7516/98/0201-0201
- Sixta, H. (2006). *Handbook of Pulp*, Wiley-VCH, Weinheim, Germany.

- Sørensen, P. A., Møllerhøj, M., and Christensen, K. A. (2015). “New dynamic models for simulation of industrial SO<sub>2</sub> oxidation reactors and wet gas sulfuric acid plants,” *Chemical Engineering Journal* 278, 421-429. DOI: 10.1016/j.cej.2014.09.023
- Teir, S., Hetland, J., Lindeberg, E., Torvanger, A., Buhr, K., Koljonen, T., Gode, J., Onarheim, K., Tjernshaugen, A., Arasto, A., *et al.* (2010). *Potential for Carbon Capture and Storage (CCS) in the Nordic Region* (Research notes 2556) VTT Technical Research Center of Finland, Espoo, Finland.
- Valeur, S., Lawler, D., Fetissoff, P., and Björklund, P. (2000). “Kraft pulp mill internal sulphuric acid production,” in: *TAPPI International Environment Conference & Exhibit*, Denver, CO, pp. 269-292.
- Valeur, S. Björklund, P., Lawler, D., and Eckert, N. (2001). “Sulphuric acid production from pulp mill non-condensable gases,” in: *International Chemical Recovery Conference*, Whistler, Canada, pp. 477-485.
- Välimäki, E., Sirén, K., and Hamaguchi, M. (2015). “Simultaneous control of sulfur and non-process elements,” *O Papel* 76(7), 59-64.
- Valmet (2017). “Control of sulfidity in a modern kraft pulp mill,” <https://www.valmet.com>.
- Valmet (2020). “Sulphuric acid plant enhances your mill chemical circulation,” <https://www.valmet.com>.
- Wallenius, J., Business Development Manager at Andritz Oy (2020). Personal communication via videoconference (04-06-2020).
- Wells, K., Pors, D., Foan, J., Chan, C., Maki, K., Kouisni, L., and Paleologou, M. (2015). “CO<sub>2</sub> impacts of commercial scale lignin extraction at Hinton Pulp using the LignoForce process & lignin substitution into petroleum-based products,” in: *PACWEST Conference*, Whistler, Canada, pp. 10-13.
- Zhu, J. Y., Chai, X.-S., Pan, X. J., Luo, Q., and Li, J. (2002). “Quantification and reduction of organic sulfur compound formation in a commercial wood pulping process,” *Environmental Science and Technology* 36(10), 2269-2272. DOI: 10.1021/es011295z

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