

NEGATIVE CARBON-DIOXIDE EMISSIONS FROM EUCALYPTUS PULP MILL INCLUDING BIOSLUDGE HTC TREATMENT

Authors: Clara Mendoza-Martinez^{1,2}, Katja Kuparinen², Mateus Martins¹, Marcelo Cardoso¹, Esa Vakkilainen², Jussi Saari²

¹Federal University of Minas Gerais. Belo Horizonte - MG, Brazil.

²Lappeenranta University of Technology - LUT Energy, Lappeenranta, Finland

ABSTRACT

Kraft pulp mills produce CO₂ for the most part in combustion processes. The recovery boiler, the biomass boiler, and the lime kiln are the largest sources of CO₂. As these CO₂ emissions originate almost entirely from burning biomass (bioenergy), the pulp mill can be considered already nearly carbon neutral as long as the wood feedstock is obtained from sustainable sources. By applying to this bioenergy use carbon capture and storage (BECCS) or use (BECCU) to permanently remove some of the carbon from circulation, pulp mills can, therefore, provide some of the negative emissions needed for climate-change mitigation. An alternative way of creating negative emissions in a pulp mill is converting process residues that are currently disposed of by landfilling or incineration into material that can serve as a stable permanent carbon storage; ideally the residues could also be converted into additional products resulting in additional revenue for the plant. In BECCS technology, the CO₂ is captured, transported, and permanently stored in an appropriate geological formation, resulting in negative net carbon dioxide emissions. In BECCU, the captured biogenic CO₂ can be used as a raw material for bioproducts. Potential processes for CO₂ utilization in pulp mills include tall oil manufacturing, lignin extraction, and production of precipitated calcium carbonate (PCC), depending on mill specificities and local conditions. CO₂ can be captured from a stream of flue gases by absorption in an aqueous solvent. Chemical absorption by alkanolamines (amine scrubbing) appears to offer an attractive alternative for CO₂ separation from combustion flue gases at pulp mills. In addition to BECCS/BECCU technologies, carbon can also be permanently removed from circulation by applying conversion technologies other than combustion on some of the biomass streams containing carbon. In the case of lignin extraction, by removing lignin from the black liquor before combustion in the recovery boiler, some of the CO₂ emissions can also be avoided altogether. Hydrothermal carbonization of the biosludge generated during primary (chemical) and secondary (biological) wastewater treatment processes is another

possibility of removing carbon in a pulp mill. The hydrochar produced is an inert substance and resistant to biological degradation. It has potential use, for example, as adsorbents for environmental applications. When mixed in soil, it can improve its carbon organic matter, reduce N₂O emissions, as well as form a permanent carbon storage. In this paper the potential of the above-mentioned technologies – post-combustion amine scrubbing for BECCU, and hydrothermal carbonization of biosludge – are evaluated.

Keywords: *Bioenergy with carbon capture and storage BECCS; Bioenergy with carbon capture and utilization BECCU; Kraft pulp mill; Climate change mitigation; Negative CO₂; Hydrothermal carbonization.*

INTRODUCTION

Anthropocene refers to the period when human activities have influenced the geological and environmental aspects at global levels [1]. The term was adopted by the Intergovernmental Panel on Climate Change (IPCC), emphasizing the negative human impact to the ecosystems [2]. One of the main concerns is climate change, with a global temperature increase of 0.85°C reported so far over the period of 1880 to 2012. According to IPCC, the atmospheric CO₂ concentration has increased by over 100 ppm (36%) in the last 250 years, from 280 ppm in the pre-industrial era to a current figure of 410 ppm [2]. Therefore, several countries signed in 2015 the Paris Agreement to reduce anthropogenic emissions in order to mitigate climate change. Maintaining global warming well below 2°C and pursuing efforts to limit temperature increase to 1.5°C above pre-industrial levels are the main objectives of the Agreement [3].

The pulp and paper industry is one of the largest energy users in the world at an estimated 5.9 EJ, while producing approximately 195 MtCO₂/year [4]. Over 80% of CO₂ emissions come from combustion of residual biomass [5]. The pulp industry has

Corresponding author: Clara Mendoza-Martinez. Lappeenranta FI-53850, Finland. Phone: +358-50-478-4024. e-mail: clara.mendoza.martinez@gmail.com

established several measures to reduce its CO₂ emissions. These include replacing fossil fuels with alternative fuels, increasing the energy efficiency of the process through waste heat recovery, among others. Although effective, these measures alone are not sufficient to achieve the established CO₂ emission reduction rates targeted. Bioenergy with carbon capture and storage (BECCS) or utilization (BECCU) technologies have been identified as some of the most promising and potentially cost-effective negative emission technologies (NETs) to mitigate carbon emissions. After being captured, the concentrated CO₂ can be pressurized and stored in underground deposits, or used for the production of fuels, chemicals, tall oil manufacturing, lignin extraction, or production of precipitated calcium carbonate (PCC).

In the chemical pulp industry, sulphate (kraft) pulping is the most common method, accounting for up to 80% of the global pulp production. Like in many industries, significant amounts of byproducts and waste are also produced. Some of these can be used profitably, i.e., transport fuel from tall oil or energy production from bark and sawdust. However, all end products cannot be reused or disposed easily. The biosludge produced in the pulp industry is an example of a challenging side stream that is neither valuable raw material nor easy to dispose of. Biosludge has accounted for over 50% of overall wastewater treatment costs in some mills. It is typically disposed in landfills, composting, or burning in the recovery or biomass boiler, all of which can be in some ways problematic. Environmental legislation also sets requirements for industries to achieve environmental targets, prompting the search for alternative solutions to comply with laws while maintaining or improving the competitiveness of products in the market. One way of reaching negative CO₂ emissions in a pulp mill and reduce the cost in the residual management, is treating the residues that are currently disposed of by landfilling or incineration to material that can serve as a stable permanent carbon storage. In this paper, the potential of the technologies, BECCS/BECCU and hydrothermal carbonization (HTC) as a possible route for sludge generated during primary (chemical) and secondary (biological) wastewater treatment processes, are evaluated.

CO₂ emission sources in pulp mills

Kuparinen et al. (2019) identified two main CO₂ sources in a pulp mill: the recovery boiler and the lime kiln [5]. When a biomass boiler is present, it is also a significant source of CO₂. Of these, the lime kiln is the main emission source originating from fossil fuels. In the lime kiln, calcination process takes place: calcium carbonate (CaCO₃) is heated to approximately 900°C generating CO₂ and lime (CaO) [6]. The CO₂ generated in the lime kiln thus originates both from the calcination process and fossil fuel combustion.

The role of the recovery boiler is recovering the pulping chemicals in the black liquor while simultaneously burning the organic wood residues remaining in the liquor after pulping.

Typically, fossil fuels used during startup and shutdown produce 10–20 kg CO₂/ADt [5]. Additionally, process upsets or equipment failures occasionally require burning fossil oil or gas. Some mills have a biomass boiler for burning organic residues generated in the wood processing stage, such as bark or fines, which also use fossil fuels during startup and shutdown [5].

2. METHODS

In the IPCC (2018) report, future scenarios are created in order to evaluate greenhouse gas (GHG) emissions mitigation and, of the technologies presented, BECCS/CCU is one of the most attractive [7]. According to the Global CCS Institute (2019), there are currently 19 large-scale carbon capture facilities in operation, 4 in construction and 28 in various stages of development around the globe. The total capture capacity of all large-scale carbon capture facilities at all stages of development has risen by 51% since 2017, and these technologies have recently received increased attention [8].

CO₂ capture technologies for fossil and biomass fuels are often divided in four basic categories: capture from industrial process streams, pre-combustion, oxy-combustion, and post-combustion [9]. In addition to these, chemical looping combustion is a promising technology with potentially very low parasitic losses [10]. Few detailed studies have been applied to pulp mills, however.

In pre-combustion carbon capture, oxygen is used in the gasification of fuels to produce syngas consisting mainly of H₂ and CO. The syngas is sent to a reactor where the gas-water displacement reaction takes place, forming CO₂ and H₂. After the product is desulfurized and passed through the carbon dioxide separator unit, CO₂ can be captured and H₂ used in an energy generation process [11]. The CO₂ concentration at the inlet of the separator is generally in the range of 15 to 60% dry basis. The total pressure is typically 2-7 MPa [9]. Several techniques can be used to separate the CO₂, including cryogenic separation, absorption, adsorption and membrane separation. In the pulp industry, pre-combustion systems based on black liquor gasification have been studied, but not yet demonstrated in operating plants.

In oxy-combustion, the combustion air is replaced by a mixture of oxygen (O₂) and recirculated exhaust gas (mainly CO₂ and H₂O), in which combustion temperature is controlled by the flue gas recirculation rate. The exclusion of nitrogen in the process creates a stream of highly concentrated CO₂ (>80%), allowing for more efficient capture. The oxy-combustion can be applied to the recovery boiler, bark boiler, or lime kiln, but modifications to the flue gas passages may be required. Implications on heat transfer, reactions and additional cost and auxiliary power consumption due to extra demand of oxygen should be taken into account.

Post-combustion carbon capture is a commercially available technology based on CO₂ absorption by chemical solvents.

The absorption processes make use of the reversible nature of the chemical reaction of an aqueous alkaline solvent, usually an amine-base. Various solvents have been tested, including monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) [11,12]. This solution is inserted in an absorption column which comes in contact with the CO₂ containing gas stream. In this column, at temperatures typically between 40 and 60°C, CO₂ is bound by the solvent. The ‘rich’ solvent containing the chemically bound CO₂ is then pumped to the top of a stripper (or regeneration vessel), via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at higher temperatures of 100–140°C. The ‘lean’ solvent, containing far less CO₂, is then pumped back to the absorber via the same heat exchanger, closing the loop [9]. Separation processes using solvents have some disadvantages due to the degradation of amine by SO₂, high corrosion rate of equipment and high consumption of energy during solvent regeneration. In practice, typical CO₂ recoveries are between 80% and 95%, but the exact recovery choice is an economic trade-off, since a higher recovery will lead to a taller absorption column, higher energy penalties and hence increased costs [9].

Several reports of post-combustion capture process based on absorption with alkanolamines have been found. Studies involving simulations [13–17], process optimization [18], reaction mechanisms [19], process implications [20] and pilot-plant studies [21]. In addition to studies linking post-combustion capture process with pulp mills. Onarheim et al. evaluated the performance and the economic feasibility of retrofitting post-combustion CO₂ capture to a pulp mill and an integrated pulp and board mill [22,23]. Also, Kuparinen et al. investigated the use of CC technologies integrated to pulp mills [5]. In general, the results show the potential of the application of BECCS/CCU technology in the plants, but the cost depends heavily on policy frameworks, regulations and incentives for negative emissions.

HTC as alternative liquid effluents treatment for CO₂ emission reduction

Currently, average water consumption in kraft pulp mills is approximately 60 m³/adt (air dried ton). This value tends to increase in older mills or those where there is little concern about the availability of fresh water, and tends to decrease down to 25 m³/adt in the most modern plants or those with limitations in capturing and treating water. However, it is unanimous in the industry that there is strong environmental pressure to reduce water consumption in the production of cellulose and paper. The effluents of pulp mills are rich in suspended solids, dissolved organics, color and, above all, organochlorine compounds (in factories that use chlorine lap and derivatives in bleaching), giving them high polluting potential. Liquid effluents are generated at different points in the process, woodhandling, digester, fiber line, bleaching, drying, evaporation, recovery boiler, causticization and calcination. Treatment of these liquid effluents, typically called sludge, is composed of a sequence of four distinct stages with different objectives: removal of coarse solids, removal of suspension solids, removal of biodegradable organic matter and toxicity, and color removal. Incineration in a recovery boiler is a potential way to dispose the sludge. Recovery boilers are designed for challenging fuels and have advanced monitoring and control systems, which is an advantage for sludge combustion. Sludge incineration results in some additional costs due to the moisture content, however: moisture vaporization requires a significant amount of energy, flue gas flow rate increases, boiler losses are increased, and ash transportation and treatment costs, and maintenance needs are increased. The exact costs depend on energy prices [24].

The potential to reduce the CO₂ emissions and manage residual streams of a modern eucalyptus (*Eucalyptus globulus*) kraft pulp mill located in South America has been analyzed via case studies. A simplified block diagram is showed in Figure 1.

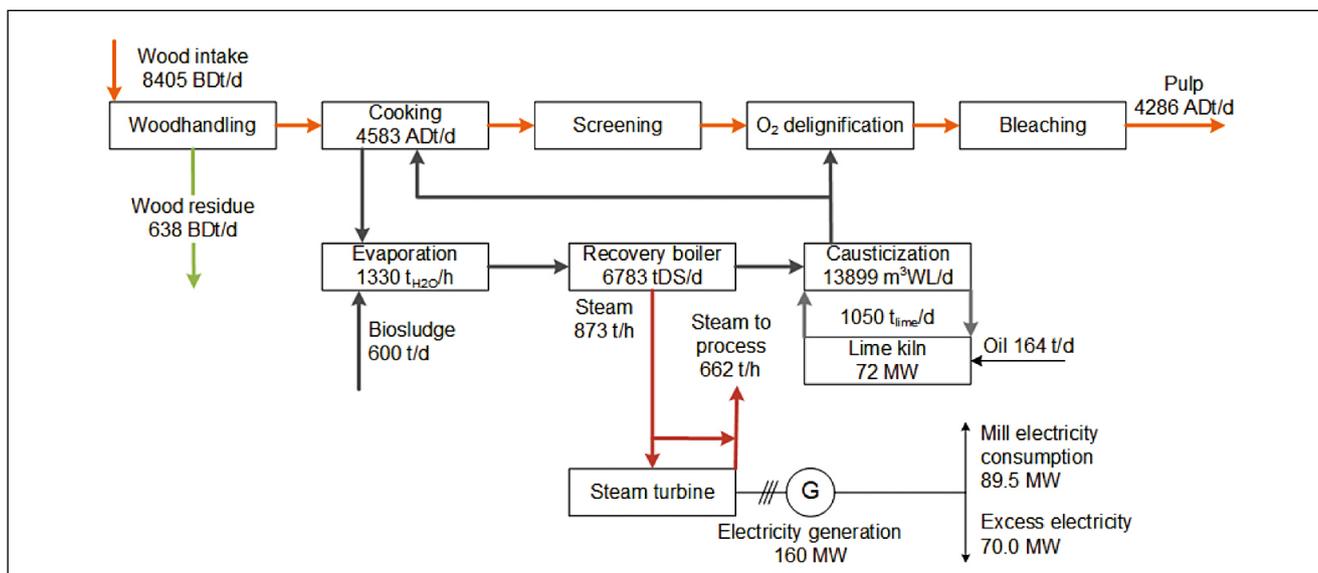


Figure 1: Flow diagram of the southern mill process in case 0

The mill considered is a large, modern stand-alone kraft pulp mill producing bleached pulp from eucalyptus. Annual pulp production is 1.5 million ADt. The sole energy source is the recovery boiler; there is no biomass boiler. The recovery boiler is able to cover the energy demand of the mill, which is typical for a modern stand-alone mill. In base case 0, CCS is assumed to be implemented via MEA scrubbing in the recovery boiler and lime kiln as in Kuparinen et al. [5].

Biosludge is dried mechanically and mixed with weak black liquor at the evaporator plant, and combusted in the recovery boiler. Biosludge production is 11.2 BDkg/ADt. Steam from the recovery boiler is used in the mill processes and for power generation in a turbogenerator. Low temperature heat flows are abundantly available to, for example, drying purposes. The electricity generation exceeds the mill's power requirements, and thus the sale of excess electricity is possible. The main operational parameters are collected in Table 1. A detailed description of the mill can be found in Hamaguchi et al. [25].

In this study, hydrothermal carbonization (HTC) of the sludge was considered instead of the traditional combustion. HTC is a mild thermochemical conversion process for biomass, taking place in a closed system at temperatures of 180–250°C and under autogenous pressure. Residence time is typically several hours. HTC offers a low emission and low waste toxicity technology for treating and upgrading diverse feedstocks. HTC treatment is suitable for high moisture content feedstock such as sludges, as no energy-intensive pre-drying is needed [26]. The process results in a hydrochar with heating value increased over that of raw sludge solids [27], while destroying

any organic pollutants. The sterile end product is suitable not only for use as an energy carrier, but also as e.g. soil conditioner, absorbent or in carbon sequestration [28,29]. The HTC process is also effective in removing alkali metals and other inorganic substances from the feedstock. Typically, the hydrochar holds 55-90% of the feedstock initial dry mass and 80- 95% of its energy content. As a solid fuel, hydrochar properties are similar to lignite [30].

The effect of biosludge HTC treatment on the energy balance of the South American kraft pulp mill is studied. The implementation of HTC is compared with traditional biosludge disposal processes (case 0), where the biosludge is combusted in the recovery boiler after introducing the sludge into black liquor in the evaporator. Two different HTC plant configurations are considered. In both, the sludge is first mechanically dewatered to 8% moisture content prior to being fed to the HTC plant. Unlike in HTC processes using solid feedstocks, no water other than the flash vapour from product slurry is added to the feed slurry; even then, the final water-to-dry ratio in the HTC reactor becomes relatively high at approximately 16:1. The HTC reactor operates at conditions of 200°C temperature and 16 bar pressure, with a three-hour slurry residence time. Mechanical dewatering to 35% wet-basis dry solids content (case A) and thermal drying to 90% dry solids (case B) was considered.

Calculations are made based on literature review, the results of laboratory-scale HTC trials conducted at LUT, and HTC process modelling. IPSEpro software was used to model the HTC unit. The HTC plant model is based on a previous study that evaluated HTC treatment of forest biomass [31]. Pulp mill balances are

Table 1. Operation parameters and main process flows of southern mill

Operational parameters		Unit	Mill
Production	Operating hours	h/a	8400
	Pulp production	ADt/d	4286
	Paper production	t/d	-
Wood handling	Wood input	BDt/d	8405
	Wood type		eucalyptus
	Residue	BDt/d	638
	Wood moisture	-	45%
Recovery boiler	Dry solids to boiler	tDS/d	6783
	Net steam flow	t/h	873
Biomass boiler	Biomass fuel use	BDt/d	-
	Net steam flow	t/h	-
Biosludge	Production	BDkg/ADt	11.2
	Production	tDS/d	48
Energy	Steam use, pulp mill	t/h	662
	Steam use, paper mill	t/h	-
	Power generation	MW	160
	Power use, pulp mill	kWh/ADt	501
	Power use, paper mill	kWh/t	-

Table 2. Energy production and consumption data of different sludge treatment cases in the southern mill

		Unit	Case 0	Case A	Case B
Sludge	Total	t/d	600	600	600
	Dry solids	t/d	48	48	48
Hydrochar	Total	t/d	-	37	96
	Dry solids	t/d	-	34	34
	Dry solids		-	90%	35%
Steam	Live steam production	t/h	873	880	880
	Mill total consumption*	t/h	662	664	663
	HTC plant consumption	t/h	-	2.68	2.06
Electricity	Gross production	MW	159.5	161.1	161.2
	Mill total consumption*	MW	89.5	89.7	89.6
	HTC plant consumption	MW	-	0.28	0.14
	Net production	MW	70.0	71.4	71.7
	Net production change	MW	0	1.39	1.68

* Includes HTC plant consumption

calculated using an updated Millflow program that includes the detailed mass and energy balances of a kraft pulp mill. Millflow was developed at LUT and presented in more detail in earlier studies [25]. During this study, an HTC unit based on the modelling was added to calculate its effect on the balances.

RESULTS AND DISCUSSION

In the southern reference mill, biosludge production is 11.2 BDkg/ADt, corresponding to 48 tds/d; in Case 0, the 600 t/d sludge flow is mixed with black liquor in the evaporation plant, and burnt in the recovery boiler. Table 2 shows the reference mill operations and the main process flows. The recovery boiler steam production of 873 t/h yields a total of 159.5 MW power generation, of which the mill consumption amounts to 89.5 MW, leaving a net excess of 70.0 MW to be sold. The mill also consumes 662 t/h extraction steam from the turbine.

When the HTC process is integrated in the mill process, the sludge is no longer sent to the evaporator plant or the recovery boiler. Figure 2 shows the main process flows in case A and

case B. HTC treatment of the sludge by Case A type plant produces low moisture char at a rate of 37 t/d. Not sending the sludge to the evaporator plant allows drying the black liquor to a significantly higher dry solids content. The net result is a clearly increased steam production of 880 t/h in the boiler, while electricity generation increases to 161.1 MW. After the 0.28 MW auxiliary power consumption of the HTC plant itself, the net electricity production of the mill increases by 1.39 MW.

The Case B HTC plant lacking the thermal drier produces a 96 t/d stream of 35% dry solids content char. While the moisture content is clearly higher than that of the char from Case A HTC plant, the evaporator capacity is similarly freed for producing higher dry solids content firing liquor, and steam generation is the same as with the Case A at 880 t/h. Although steam consumption is slightly reduced, the gross power generation is almost identical at 161.1 MW, but the slightly lower power consumption of the Case B HTC plant results in very-slightly greater net generation. Table 2 summarizes the main consumption and production of the southern pulp mill.

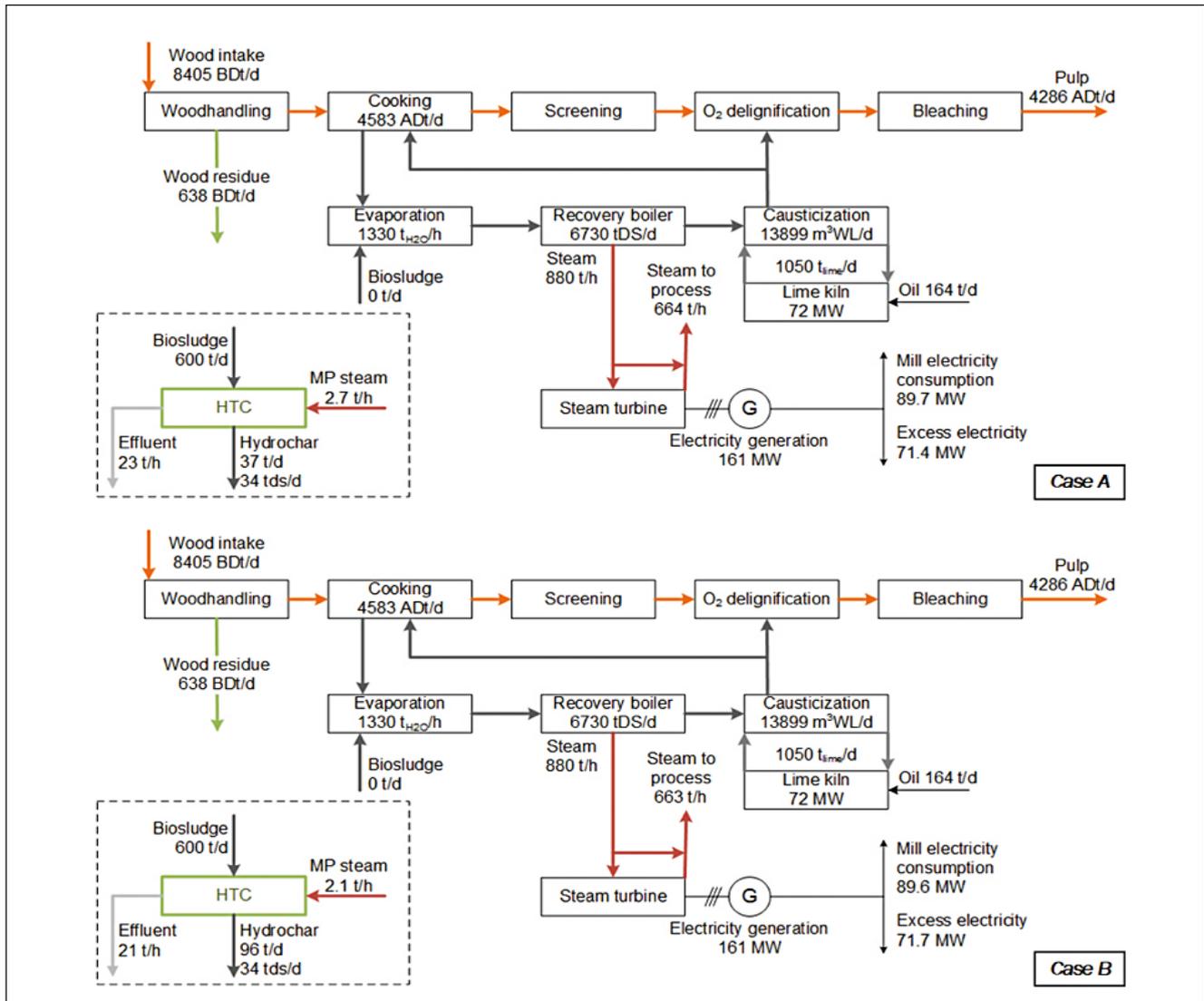


Figure 2. Flow diagram of the southern mill process in case A and case B

Not feeding high-moisture biosludge to the evaporator plant results in a positive net change in electricity generation over case 0 in both cases. If the intended end use of the hydrochar does not require thermal drying to a very low moisture content, Case B is clearly superior as it yields a 0.3 MW net power generation benefit in addition to having a simpler process without the dryer.

In general, the impact of the moisture of the biosludge on the operation of the recovery boiler is clear; this was demonstrated earlier in [32] by calculating the steam production of the boiler. When the share of biosludge is 1% total fuel mass flow rate, the steam production would change for moisture contents of 75%, 85%, and 95% are 0.16%, 0.31%, and 0.47%, respectively. The effect on the recovery boiler's operation may appear small, but in the long run the amount of lost steam is notable. The calculations also showed that the CO₂ emissions of the recovery boiler was 7524 t/d and 1099 t/d for the lime kiln [5]. The effect of carbon capture process in the energy balances, when

MEA based post-combustion process is used to capture CO₂ from recovery boiler flue gas, was 2378 t/d for case 0. In the HTC integration, when biosludge is combusted in the recovery boiler it increases the boiler load. If the recovery boiler is the bottleneck of the pulping process, biosludge disposal using other methods enable pulp production increase, HTC treatment offers, however, also other utilization possibilities for biosludge in addition to combustion. HTC has previously been presented as a method to produce for example activated carbon, and HTC-treated biomass can be used as soil conditioner, unlike untreated biosludge. Biosludge typically includes e.g. nitrogen and phosphorous that are needed in fertilizers [33,34].

CONCLUSIONS

The growing concern with the environmental impacts generated in pulp mills has been inducing the development of new methods that help to understand, control and, or reduce these impacts. The life cycle analysis of products, processes and

activities have proven to be an important tool in helping studies of this nature, considering the environmental impact throughout the product's life cycle: from the extraction of the raw materials used to the production, use and final disposal of the product. BECCS/CCU is an attractive technology for climate change mitigation and can be a source to reach negative CO₂ emissions in kraft pulp mills. In the case of a modern pulp mill, relatively small amount of carbon capture and storage could make a pulp mill a carbon sink instead of a carbon source. If HTC-treated biomass is used as soil conditioner, the carbon in the biosludge

is then stored and not released in the atmosphere. For a pulp mill, this can offer a way to get closer to negative emissions.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support from the Academy of Finland.

Open access funding provided by Lappeenranta University of Technology (LUT). This study was funded by the Academy of Finland under the project "Role of forest industry transformation in energy efficiency improvement and reducing CO₂ emissions". ■

REFERENCES

1. Crutzen, P., Stoermer, E., "The Anthropocene IGBP newsletter 41", R. Swedish Acad. Sci. Sweden. (2000).
2. PCC, "Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change". (2014).
3. United Nations, "Summary of the Paris Agreement", United Nations Framew. Conv. Clim. Chang. (2015).
4. IEA, "Energy Technology Perspectives 2017", (2017).
5. Kuparinen, K., Vakkilainen, E., Tynjälä, T., "Biomass-based carbon capture and utilization in kraft pulp mills", *Mitig. Adapt. Strateg. Glob. Chang.* (2019).
6. Ontiveros-Ortega, E., Ruiz-Agudo, E.M., Ontiveros-Ortega, A. "Thermal decomposition of the CaO in traditional lime kilns. Applications in cultural heritage conservation", *Constr. Build. Mater.* (2018).
7. IPCC, "Summary for Policymakers. Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels". (2018).
8. Global CCS Institute, "Global Status of CCS 2019", (2019).
9. IPCC, "Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change", *Environ. Sci. Technol.* (2005).
10. Saari, J., Peltola, P., Tynjälä, T., Hyppänen, T., Kaikko, J., Vakkilainen, E. "High-efficiency bioenergy carbon capture integrating chemical looping combustion with oxygen uncoupling and a large cogeneration plant", *Energies.* (2020).
11. Nemitallah, M.A., Habib, M.A., Badr, H.M., Said, S.A., Jamal, A., Ben-Mansour, R., Mokheimer, E.M.A., Mezghani, K. "Oxy-fuel combustion technology: current status, applications, and trends", *Int. J. Energy Res.* (2017).
12. Cormos, A.M., Cormos, C.C. "Reducing the carbon footprint of cement industry by post-combustion CO₂ capture: Techno-economic and environmental assessment of a CCS project in Romania", *Chem. Eng. Res. Des.* (2017).
13. Li, B.H., Zhang, N., Smith, R. "Simulation and analysis of CO₂ capture process with aqueous monoethanolamine solution", *Appl. Energy.* (2016).
14. Garcia, M., Knuutila, H.K., Gu, S. "ASPEN PLUS simulation model for CO₂ removal with MEA: Validation of desorption model with experimental data", *J. Environ. Chem. Eng.* (2017).
15. Enaasen Flø, N., Knuutila, H., Kvamsdal, H.M., Hillestad, M. "Dynamic model validation of the post-combustion CO₂ absorption process", *Int. J. Greenh. Gas Control.* (2015).
16. Biliyok, C., Lawal, A., Wang, M., Seibert, F. "Dynamic modelling, validation and analysis of post-combustion chemical absorption CO₂ capture plant", *Int. J. Greenh. Gas Control.* (2012).
17. Harun, N., Nittaya, T., Douglas, P.L., Croiset, E., Ricardez-Sandoval, L.A. "Dynamic simulation of MEA absorption process for CO₂ capture from power plants", *Int. J. Greenh. Gas Control.* (2012).
18. Mores, P., Scenna, N., Mussati, S. "CO₂ capture using monoethanolamine (MEA) aqueous solution: Modeling and optimization of the solvent regeneration and CO₂ desorption process", *Energy.* (2012).
19. Matsuzaki, Y., Yamada, H., Chowdhury, F.A., Higashii, T., Onoda, M. "Ab initio study of CO₂ capture mechanisms in aqueous monoethanolamine: Reaction pathways for the direct interconversion of carbamate and bicarbonate", *J. Phys. Chem. A.* (2013).
20. Luis P., "Use of monoethanolamine (MEA) for CO₂ capture in a global scenario: Consequences and alternatives, Desalination". Master thesis, Lappeenranta University of Technology (2016).
21. Notz, R., Mangalapally, H.P., Hasse, H. "Post combustion CO₂ capture by reactive absorption: Pilot plant description and results of systematic studies with MEA", *Int. J. Greenh. Gas Control.* (2012).
22. Onarheim, K., Santos, S., Kangas, P., Hankalin, V., "Performance and costs of CCS in the pulp and paper industry part 1: Performance of amine-based post-combustion CO₂ capture", *Int. J. Greenh. Gas Control.* (2017).
23. Onarheim, K., Santos, S., Kangas, P., Hankalin, V., "Performance and cost of CCS in the pulp and paper industry part 2: Economic feasibility of amine-based post-combustion CO₂ capture", *Int. J. Greenh. Gas Control.* (2017).
24. Lehtinen P., "Metsäteollisuuden lietteiden bioterminen kuivaus (Bio thermal drying of sludge in forest industry). (In Finnish)". Master's thesis., Lappeenranta University of Technology. (2001).
25. Hamaguchi, M., Vakkilainen, E.K., Ryder, P., The impact of lignin removal on the dimensioning of eucalyptus pulp mills, *Appita J.* (2011).
26. Alatalo, S.M., Repo, E., Mäkilä, E., Salonen, J., Vakkilainen, E., Sillanpää, M. "Adsorption behavior of hydrothermally treated municipal sludge & pulp and paper industry sludge", *Bioresour. Technol.* (2013).
27. Child, M. "Industrial-Scale Hydrothermal Carbonization of Waste Sludge Materials for Fuel Production", Thesis. (2014).
28. Libra, J.A., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., Titirici, M.M., Fühner, C., Bens, O., Kern, J., Emmerich, K.H. "Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis", *Biofuels* (2011).
29. Funke, A., Ziegler, E., "Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering", *Biofuels, Bioprod. Biorefining.* (2010).
30. Sermyagina, E., Saari, J., Kaikko, J., Vakkilainen, E., "Hydrothermal carbonization of coniferous biomass: Effect of process parameters on mass and energy yields", *J. Anal. Appl. Pyrolysis.* (2015).
31. Saari, J., Sermyagina, E., Kaikko, J., Vakkilainen, E., Sergeev, V. "Integration of hydrothermal carbonization and a CHP plant: Part 2 –operational and economic analysis", *Energy.* (2016).
32. Harila, P., Kivilinna, V.A., "Biosludge incineration in a recovery boiler", *Water Sci. Technol.* (1999).
33. Feagley, S.E., Valdez, M.S., Hudnall, W.H. "Papermill Sludge, Phosphorus, Potassium, and Lime Effect on Clover Grown on a Mine Soil", *J. Environ. Qual.* (1994).
34. Kost, D.A., Boutelle, D.A., Larson, M.M., Smith, W.D., Vimmerstedt, J.P. "Papermill Sludge Amendments, Tree Protection, and Tree Establishment on an Abandoned Coal Minesoil", *J. Environ. Qual.* (1997).