

Value creation by converting pulp mill flue gas streams to green fuels

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ABSTRACT: Climate change mitigation induces strong growth in renewable electricity production, partly driven by shifts in environmental policies and regulation. Intermittent renewable electricity requires supporting systems in the form of sustainable hydrocarbon chemicals such as transportation fuels. Bulk chemical production fits well into a pulp mill environment, given their large volumes, stable operation, and ample supply of biomass-based carbon feedstock in the form of flue gases. Until now, the utilization of the flue gases from conventional operation of a pulp mill has received little attention. Harnessing these flue gases into usable products could offer additional value to mill operators, while also diversifying their product portfolio. However, electricity-based fuels and products require extra energy in the conversion step and may not be commercially competitive with current fossil products under the current regulation. There might also be uncertainties about future commodity prices. Thus, the objective of this study is to estimate the economic competitiveness and the added value of selected side products that could be produced alongside conventional pulp and paper products.

A typical modern pulp mill is modeled in different product configurations and operational environments, which allows testing of various development paths. This illustrates how the overall energy and mass balance of a pulp mill would react to changes in different final products and other parameters. The focus of the study is in synthetic methanol, which is produced from flue gases and excess resources from the mill, with minimal interference to the pulping process. The results aid in assessing the necessity and magnitude of a premium payment for subsidizing green alternatives to replace current fossil fuels and chemicals. Additionally, the results function as an indicator of the development state of the pulp and paper industry in the turmoil of climate change regulation. The results indicate that power-to-X systems offer one more viable pathway alternative for broadening the product portfolio of the pulp and paper sector, as well as opening new flexibility measures and services to grid stabilization. Market conditions were found to have a significant impact on the perceived profitability.

Application: The study presents an economic evaluation of a power-to-methanol process integrated into a pulp mill environment. The study evaluates the mass and energy balance for a process where the flue gases of the pulp mill would be converted into methanol using a synthesis process.

One of the most urgent tasks of climate change mitigation is to prevent the release of additional greenhouse gases, most importantly fossil carbon dioxide (CO₂) [1]. To enact the climate agreements on a practical level, novel emission reduction measures are required in collaboration with effective carbon pricing schemes and regulation.

Energy-intensive industries have a large role in implementing emission reductions, not only by reducing energy intensity and by switching to sustainable energy sources, but also by recycling waste streams into useful products. This process is commonly referred to as carbon capture and utilization (CCU), and it could help to offset emissions from other sectors, which may be difficult to otherwise decarbonize. Flue gases from combustion can be processed into fuels or chemicals and used directly to replace fossil products in order to reduce greenhouse gas emissions. The principle is based on the treatment of the flue gases to extract CO₂, which is then typically combined with hydrogen into a useful end product.

The environmental impact of CO₂-based fuels and chem-

icals may be assessed using standardized life cycle assessments, although individual assessments are often not comparable due to different methodological choices [2]. The emission burden of hydrogen is typically identified as a dominating factor, which is why renewable or low-carbon electricity is a necessity when electrolysis-sourced hydrogen is employed [3-7]. Intuitively, CCU processes may be described as carbon-neutral, carbon-positive, or even carbon-negative, depending on the origin of the CO₂ and overall emissions released during the process. Life cycle assessments might also yield negative values for the environmental impact, but its meaning is very different and only applies when compared to a reference case [2]. Defining clear yet adequately simplified regulatory guidelines for CO₂-based fuels and chemicals is difficult. For instance, an IRENA report defines that e-methanol is green only if the CO₂ originates from biomass or directly from atmosphere [8]. Methanol using fossil CO₂ could be termed to be low-carbon, but not green or renewable. In the EU legislation, the RED II proposal and its specific calculation rules are

not yet clear on the requirements and impact of CO₂ origin or even about electricity use, but with great uncertainty one could make the presumption that the origin of the CO₂ “is not relevant for determining emission saving” [9].

A pulp mill environment offers a lucrative framework for producing CO₂-recycled renewable fuels and chemicals due to numerous reasons. First, a large portion of the flue gas emissions from pulp mills can originate from biomass, although this is dependent on the configuration of the mill. Some mills may be using fossil fuels extensively, whereas others are based purely on biomass and biofuels. Bio-based feedstock decreases the phase-out risk which may be present for other fossil energy using sites (e.g., coal power or conventional steel) in the medium and long-term. A variation of the same argument may be formulated by saying that bio-CO₂ does not share a similar risk of fossil lock-in [10] as does integration with fossil CO₂ sources. Additionally, the facilities typically operate using high capacity factors that reduce the relative impact of capital expenditures. Moreover, there are possibilities to integrate resources and processes such as process heat, electricity, waste disposal, or feedstock pretreatment. Finally, the marketability, legislative status, and brand of the product may be better with a bio-based feedstock. Coupling pulp mills with carbon capture and utilization schemes can therefore be beneficial from an economic and environmental point of view, as well as for reducing investment risk.

The objective of this work is to assess the viability of renewable fuel and chemical production linked with pulp mills, particularly with methanol synthesis and water electrolysis. Specifically for pulp mills, there are a number of different pathways that are available for producing low-carbon products [11]. An overarching pathway summary for the electrification of the chemical industry and carbon dioxide hydrogenation may be found from previous works [12,13]. Previous studies have evaluated the economic profitability of carbon utilization schemes for different products and environments. Techno-economic assessments have been performed for methanol before [14], assuming a fixed price for input hydrogen and methanol market value, which resulted in non-profitable operation. The approach of this work enables a more holistic assessment of the profitability aspect under fluctuating market conditions by allowing price variations. Similar techno-economic sensitivity analyses have been performed using CO₂ from a coal power plant and hydrogen from electrolysis using hydropower [15], concluding that profitability may be reached with a suitable combination of methanol market price and hydrogen acquisition costs. Numerous studies have also simulated technical integration and economics of various methanol production schemes linked with power production units [16-19], solar-thermal energy [20], biogas [21], industrial processes linked with chlor-alkali production [22], steel refining [23-26], and sugar mills [27]. However, apparently very few research articles have specifically focused on integration with a pulp

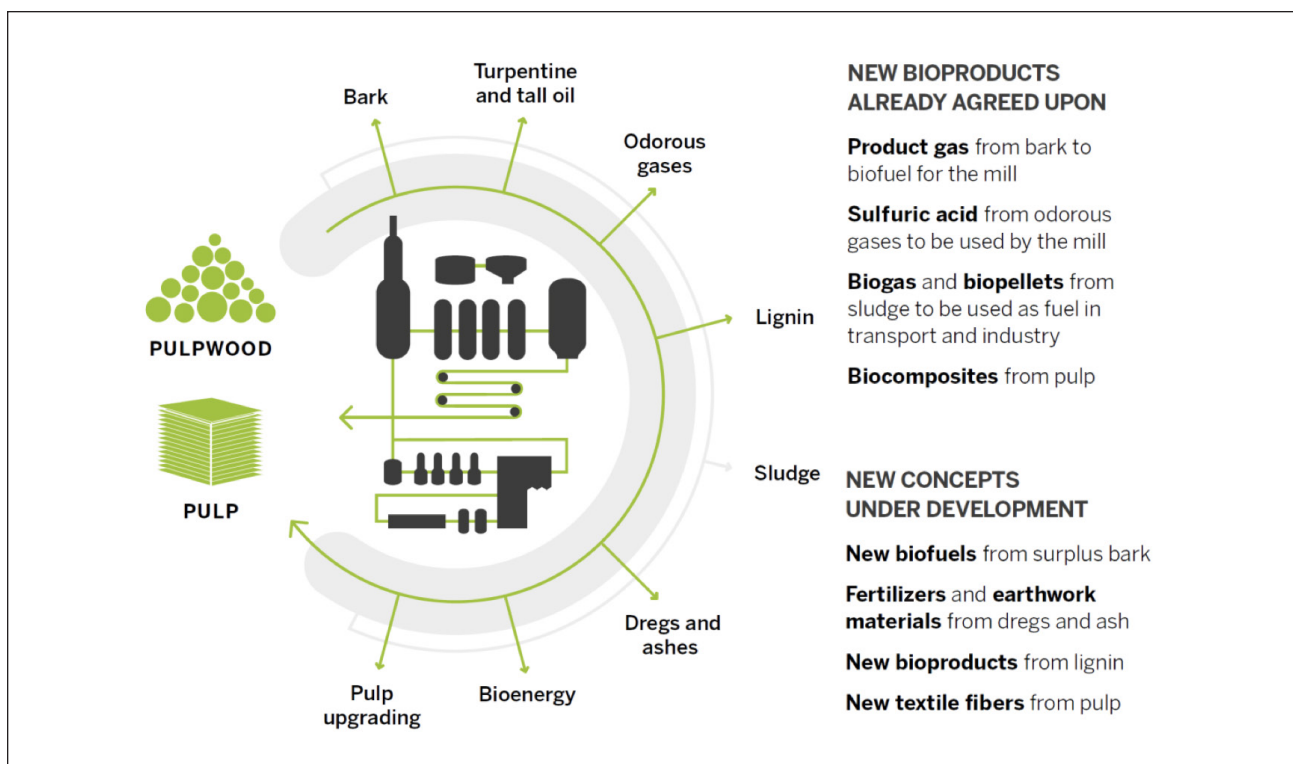
mill, excluding systems employing biomass or black liquor gasification-based pathways [28-31]. The proposed plant configuration in black liquor gasification systems can be considered significantly different from the electrolytic pathway investigated in this work. The novelty of this work is thus the application of carbon dioxide hydrogenation in a pulp mill environment, by utilizing the flue gases of the process with minimal impact on the original pulp process. A unique approach is also used for the profitability assessment by using a reference case that may be adjusted for different electricity and methanol market prices. These cost and profitability estimations may be used to evaluate different strategical alternatives, which are then pursued in more detail in more accurate estimations.

PULP MILL PRODUCT PORTFOLIO

A modern pulp mill produces several additional products from the side stream in addition to the pulp (**Fig. 1**). As an example, Metsä Group's bioproduct mill in Äänekoski, Finland, utilizes bark in a gasifier that fires the lime kiln, and sludge is converted to biopellets and biogas. In addition, sulfuric acid is produced from odorous gases of the mill for internal use, and pulp can be used for biocomposites and textile fibers. Furthermore, several new concepts are under development: new biofuels from surplus bark, fertilizers and earthwork materials from the dregs and ash, and new bioproducts from lignin. The Äänekoski bioproduct mill is already deriving 20% of its revenue from bioproducts other than pulp [33]. Another example of additional production is the integrated biodiesel production at the UPM Lappeenranta Mill in Finland [34]. As seen from these examples, pulp mills are developing to resemble biorefineries that produce multiple valuable commodities besides the traditional pulp and paper products.

The energy efficiency of European pulp and paper mills has increased by 22.4% from 1991 to 2017 [35]. Modern mills can export vast amounts of energy; for instance, the Äänekoski mill produces 240% of its energy demand, or 1.8 TWh in total. The surplus electricity is exported to the Finnish national grid, providing 2.5% of the nation's energy as bioelectricity [33]. Aside from numerous energy efficiency improvements, Äänekoski's high energy output is also influenced by the high power recovery boiler supplied by Valmet. The electricity production per dry solids (ds) ton of black liquor (BL) has increased by 22.5 % compared to the level of early 1990s (4.35 kg_{steam}/kgBL_{ds}) [36].

A varying electricity price enables profitable avenues for business in the form of load response services, which are also applicable for pulp mills. Intelligent scheduling of mechanical pulping can give 5%–20 % monetary savings [37]. In Finland, the disturbance reserve market for frequency control is available for a price of 1.9 €/MW/h (2020). For the active frequency controlled normal reserve, the price is 13.5 €/MW/h [38]. This requires more complicated and active control of the pulpers.



1. Metsä Group's new bioproduct mill in Äänekoski, Finland, utilizes 100% of the side streams [32].

Several new applications are under development for further improvements in energy efficiency and environmental impacts of pulp mills. Steam explosion pretreatment improves the energy density, pelletization properties, and the grindability of the surplus bark [39]. The trademarked LignoBoost technology enables extraction of lignin from black liquor. The produced lignin can be used for firing the lime kiln or applied as a chemical [40]. Regarding the recovery boiler, nitrogen oxide (NO_x) scrubbers provide ultra-low emissions. The mill-wide optimization of pulp mills provides significant savings in chemical and energy costs [36]. The increased amount of surplus electricity may also be converted to synthetic energy carriers, for instance methanol, that could be applied in the substitution of fossil fuels.

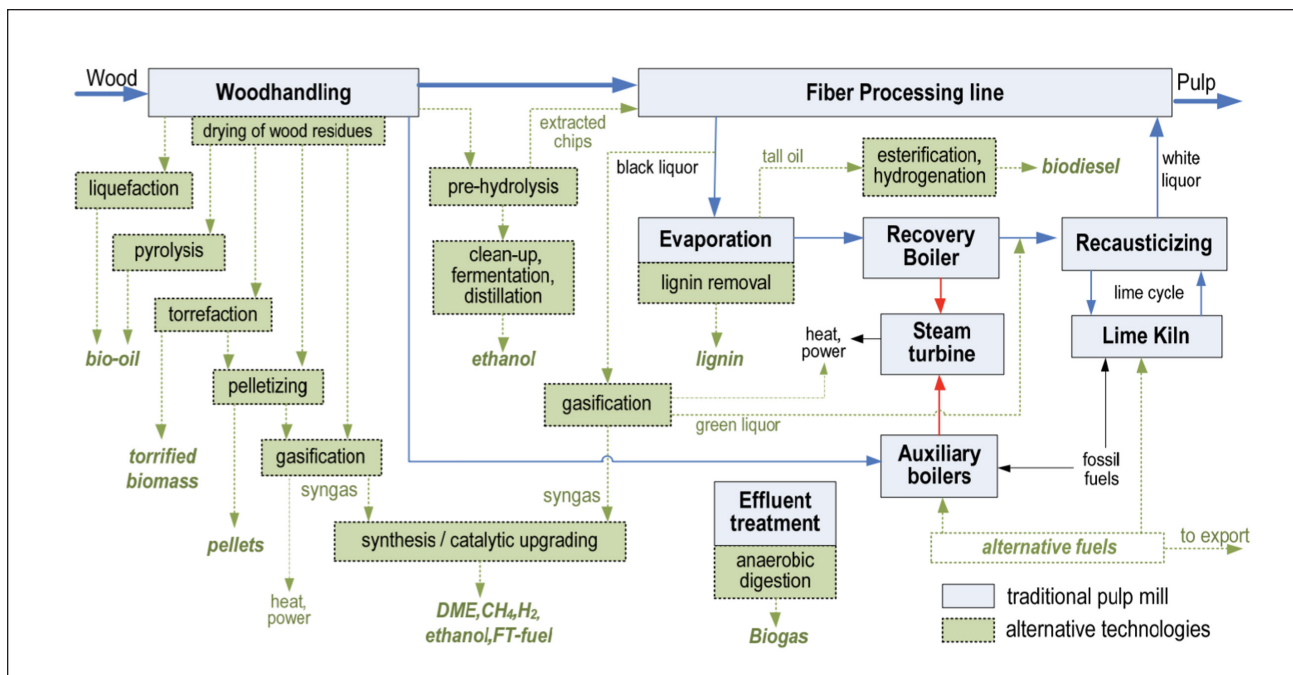
RENEWABLE FUEL PRODUCTION IN PULP MILLS

Alternative renewable fuels can be produced either by directly processing biomass (biofuels), or by an indirect route using renewable electricity and carbon as a feedstock (electrofuels or e-fuels, power-to-X, PtX). Another commonly used term is synthetic fuels. A common form of carbon feedstock is the mixture termed *syngas*, which consists of carbon monoxide, hydrogen, and often also CO_2 . The ambiguity of the term arises from the fact that syngas may be produced from a variety of sources, including coal or biomass through gasification, natural gas by utilizing steam methane reforming, or from practically any carbon-containing flue gas stream by using a reverse water-gas shift reac-

tion in the presence of additional hydrogen. There are also direct fuel conversion processes that do not require the intermediate step of syngas production. Feedstocks for these processes include CO_2 , hydrogen, and a variety of intermediate products such as methanol or dimethyl ether (DME).

Biofuel production that is directly integrated into a pulp mill can be based on the wood handling step, black liquor processing, or effluent treatment (**Fig. 2**) [41]. In this work, however, the focus is on indirect integration, which involves CO_2 capture from flue gases and subsequent hydrogenation into renewable methanol. The process requires auxiliary energy input, most importantly in the form of electricity for hydrogen generation. The required power can be obtained from the pulp mill, or alternatively from other co-located renewable sources such as photovoltaics or wind power.

The CO_2 extracted from the flue gases of these plants could produce significant quantities of biofuels in local scale. For instance, Sweden could cover the whole demand of road transport by electrofuels from biogenic CO_2 sources, with the majority coming from pulp and paper mills [42]. Available electricity has been identified as a challenge and bottleneck of the process [42-44], although regional discrepancies can be rather large. Globally, CO_2 supply from industrial sources has been projected to be insufficient past 2030, meaning that direct air capture would be essential [45]. Other studies have hypothesized that chemical conversion of CO_2 will have only a marginal role in climate change mitigation [46].



2. The kraft pulp mill and the alternative technologies for biofuels production [41].

As some pulp mills use significant quantities of biomass as the raw material, a possibility exists for producing low-carbon fuels and chemicals in scale without requiring large increases in land use for forestry or additional logging. Direct emissions reductions can be obtained on the medium term, provided that the products replace fossil alternatives. So far, the pulp industry has shown little interest towards synthetic fuel production and PtX systems, despite its clear benefits in climate mitigation and huge market potential. It can be speculated that this is partially caused by a lack of an incentive to capture emissions, because biogenic emissions are so often neglected in various carbon pricing schemes. Furthermore, supportive long-term commitments, targets, and policies, such as advanced biofuel targets or quota obligations, would need to be in place to enhance the deployment of biorefineries and the bioeconomy [47]. Another reason for the slow development is the relatively poor profitability of PtX schemes. The cost-competitiveness of power-to-methanol is not that favorable against fossil methanol [14,15], and previous studies have estimated that a green premium of 60%–112% relative to fossil price would be required [48,49]. More valuable chemicals, such as formic acid, could be profitable, but face other challenges with limited market size and low technological readiness level [50]. Methanol can be used as an intermediate product for various other chemicals, including formaldehyde, DME, gasoline, diesel, and jet fuel [14,48].

Pulp mills are often located in remote and woody areas, and a recent expansion trend is showing a high concentration of mill projects in developing countries (Fig. 3). Electricity grid connections in developing countries are sometimes poor, which can cause congestion and hinder

electricity transmission. Pulp mills produce additional heat, which is typically converted into electricity. With poor electricity grid infrastructure, this could be problematic.

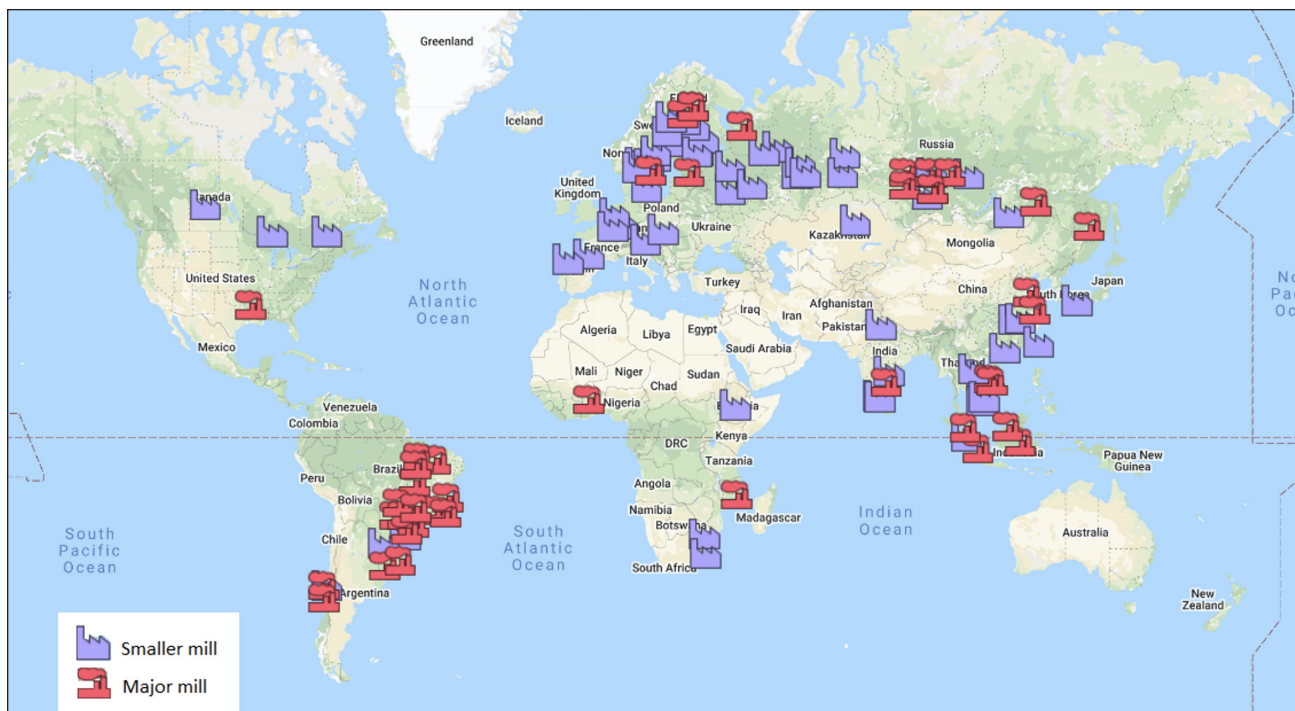
In addition, grid improvement projects can be very costly due to large distances and rough terrain, which has led to alternative investment decisions, such as the integration of chemical production at the pulp mill site [52]. The need to export electricity to the grid can, in such cases, be reduced or avoided completely by diverting some of the excess electricity to manufacturing of chemicals. Thus, there is no need to limit the capacity of the pulp plant, and the resources of the pulp mill are used effectively. The PtX production is highly electricity-intensive, mostly due to the hydrogen production step using electrolyzers. As such, PtX offers yet another option for converting excess electricity into valuable commodities.

Carbon dioxide capture

Carbon dioxide capture technology is used to obtain the carbon-component for the fuel production. In this work, amine gas treating is used, with monoethanolamine (MEA) as the working fluid. It is the most mature CO₂ capture technology currently available.

In the process, as shown in Fig. 4, flue gas enters the bottom section of the adsorption column, whereas the MEA solvent is introduced to the top of the container and allowed to react with the gas. The CO₂-rich solvent then passes a preheater and travels through the regeneration column, where the MEA-solvent is extracted and sent back to the adsorption column. The CO₂ stream is then dehydrated and compressed as it leaves the cycle [18].

The process requires heat for the desorption and regen-



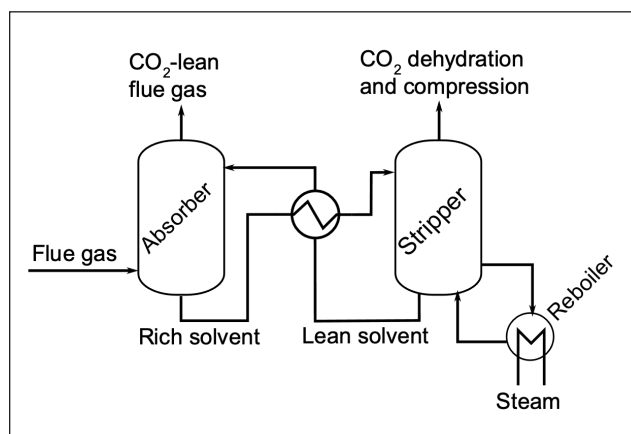
3. Planned and proposed new pulp capacity globally. Major (over 400,000 metric tons/year) and smaller mills (100,000 metric tons/year) are included [51].

eration of the solvent. Furthermore, the compression of the captured CO_2 to the working pressure of the synthesis is required. Some electricity is used to circulate the MEA-solvent in the process. In addition, some makeup solvent is required due to degradation and to replace losses in slip streams.

Electrolysis

In 2013, 86% of global hydrogen originated from fossil sources, mostly from reforming of natural gas [53]. Electrolysis could be used to produce low-carbon hydrogen, but so far the technology shift to sustainable production has been slow. There are three major types of electrolyzers: alkaline electrolyzer (AEL), proton exchange membrane (PEM), and solid oxide electrolyzer cell (SOEC). Alkaline electrolyzer is the most mature and proven technology to date. Efficiency of such electrolyzers lies between 60%–80%, when defined as the ratio between electrical energy to higher heating value of hydrogen [53]. Residual heat from the electrolyzer is available at temperatures of 70°C–90°C. Pulp mills often have residual low-quality heat streams already available, so the utilization of electrolyzer heat was not considered in this work.

Hydrogen production also produces oxygen, which could be utilized at the pulp mill in bleaching. A 10 MW electrolyzer produces roughly 1.5 tons of oxygen per hour. The oxygen demand of a pulp mill is dependent on the configuration of the mill, with a range of 20–35 kg/air-dried (a.d.) metric ton being quite typical [54]. For the reference



4. Schematic of amine-absorption-based CO_2 capture process.

mill studied in this paper, oxygen demand would thus lie between 3.8 to 6.6 tons/h with the previous specific oxygen consumption. In conclusion, if the oxygen demand is used as a dimensioning parameter for the electrolyzer, its scale will remain rather small in proportion to the available resources (i.e., electricity production) available heat for CO_2 capture and CO_2 flow.

Methanol synthesis

The predominant pathway for producing methanol is a two-step process, involving an initial reforming of natural gas to obtain syngas, which is then hydrogenated to methanol in the second stage of the process. Methanol can also be pro-

duced in a single-step process directly from CO₂ [16]. In this work, a direct one-step methanol synthesis is applied.

According to the stoichiometric equation of methanol synthesis (Eq. 1), a portion of the reacting hydrogen is not bound to the methanol, but instead forms water. As such, the stoichiometric efficiency of the reaction is 86%, based on the higher heating values of hydrogen and methanol. The combined theoretical efficiency of the whole process, from electricity to methanol, is then roughly 64% when the losses in the electrolyzer are also accounted for. The synthesis reaction itself is exothermic, and it can supply about a third of the heat required in the CO₂ capture process during absorbent regeneration [18].



METHODS

A technoeconomic calculation is used to compare the performance of different pulp mill configurations. A reference system represents a large modern pulp mill, with annual pulp production of 1.5 M a.d. metric tons/year. The studied system is modified from the reference by diverting excess electricity and heat to the methanol production process, instead of selling the excess to the grid. A case study with four alternative configurations is investigated:

1. Base case. No methanol is produced.

2. Restricted base case. No methanol is produced, but electricity sales are also limited to 30 MW. This case is included to simulate a scenario where the local electricity grid is limited in its capability to transfer large amounts of electricity.

3. Methanol case. All excess electricity is used to produce methanol, and electricity is not exported to the grid at all. Pulp and paper production is not affected by this change.

4. Hybrid case. Only a part of the electricity is converted into methanol, whereas the rest is still sold to grid as in the reference case. Methanol production can thus be adjusted based on the market price of electricity.

Reference pulp mill

The reference pulp mill is modeled to represent a modern kraft pulp mill located in Northern Europe and using softwood as the raw material. The mill calculations were carried out using the updated Millflow program, which is a mill spreadsheet including detailed mass and energy balances. Millflow has been developed at LUT University and is presented in more detail in earlier works [55,56]. The model has been in development and use for over a decade, and it includes a comprehensive energy balance evaluation tool. The calculations of the model are based on scientific literature references and data from real operating mills, as well as practical experience from the industry and different projects. The results have been previously verified in collaboration with pulp and paper companies using real op-

Electricity and energy flows		
Excess electric energy	1355	GWh
Excess heat energy	4090	GWh
CO ₂ sources		
Power boiler	0.60	Mt _{CO₂} /year
Recovery boiler	2.47	Mt _{CO₂} /year
Lime kiln	0.46	Mt _{CO₂} /year
Total	3.53	Mt _{CO₂} /year
CO ₂ = carbon dioxide; Mt _{CO₂} = million metric tons CO ₂ .		

I. Available resources at the reference mill.

erating values of existing mills. The model has also been compared with other pulp models (e.g., WinGems [57,58]).

The reference mill model is based on an earlier Northern mill model, which is explained in more detail in an earlier publication [59]. Modifications were done for this study by removing paper production and increasing the pulp production to 1.5 M a.d. metric tons. The mill generates steam in a recovery boiler and in a power boiler, where black liquor and residue from wood handling are incinerated. In addition to these, the lime kiln combusting fossil oil is a large point source of CO₂. As a standalone mill, the reference mill produces a high share of excess electricity and heat that can be sold or used for other purposes, such as process integration options. **Table I** presents the process values that are most relevant for the studied methanol system. The studied system utilizes available resources from the mill, with minimal interference to the actual pulping process and without affecting pulp production and quality.

Methanol production

Additional equipment is necessary to manufacture methanol from the flue gases of the pulp mill. The technological description of the equipment was given earlier in the “Renewable Fuel Production in Pulp Mills” section. Key financial parameters of relevant components are shown in **Table II**, and other relevant simulation parameters are shown in **Table III**.

Capital investments (*C*) of each component *k* (i.e., CO₂ capture, electrolysis, methanol synthesis) are converted into annual payments by using a capital recovery factor. The overall cost of produced methanol (*P*) can then be estimated on an annual basis by using Eq. 2. The term *O* refers to annual operation cost, *Q* to the annual quantity of methanol produced, *r* is the interest rate, and *n* is the lifetime of the unit. Only the additional investments are taken into account in methanol price; the pulp mill itself is considered to be profitable on its own and its costs are not considered to be a part of the investment.

Synthesis CAPEX	6000	€/kgMeOH/h	[14]
Synthesis OPEX	5	% of capital investment	
Electrolyzer CAPEX	850	€/kW	[60]
Electrolyzer OPEX	2	% of capital investment	[60]
CO ₂ capture CAPEX	3000	€/kgCO ₂ /h	[61]
CO ₂ capture OPEX	4	% of capital investment	[61]
District heat price	10	€/MWh	
Methanol price	400	€/metric ton	[61]
Interest rate, WACC	6	%	
Plant lifetime	15	years	
Full load hours	8000	hours	

CAPEX = capital expenditures; OPEX = operating expenditures; WACC = weighted average cost of capital.

II. Financial parameters of relevant components in methanol (MeOH) production.

Synthesis			
CO ₂ conversion	93	%	[14], [62]
Auxiliary electricity consumption	170	kWh/tMeOH	[14], [62]
Specific heat production	430	kWh/tMeOH	[14], [62]
Electrolyzer			
System efficiency	52.5	MWh _{el} /tH ₂	[53], [63]
CO ₂ capture			
Heat consumption in regeneration	1000	kWh/tCO ₂	[61]
Auxiliary electricity consumption	250	kWh/tCO ₂	[61]

kWh/tMeOH = kilowatt hours per metric tons of methanol; MWh_{el}/tH₂ = megawatt hours of electricity per metric ton of hydrogen; kWh/tCO₂ = kilowatt hours per metric tons of carbon dioxide.

III. Additional relevant simulation parameters.

$$P = \frac{\sum_{k=1}^n C_k \cdot \frac{r(1+r)^n}{(1+r)^n - 1} + O_k}{Q} \quad (2)$$

Methanol prices in Europe and the United States have fluctuated between 200 and 500 €/metric ton in recent years [64]. However, in the case of pulp mills, the produced methanol could have a higher market value, since both the electricity and carbon source could be based on renewable biomass. The price of heat is assumed rather low in this work, as its importance can be limited, especially in warmer climates. Electricity and methanol price are variable in some of the calculations.

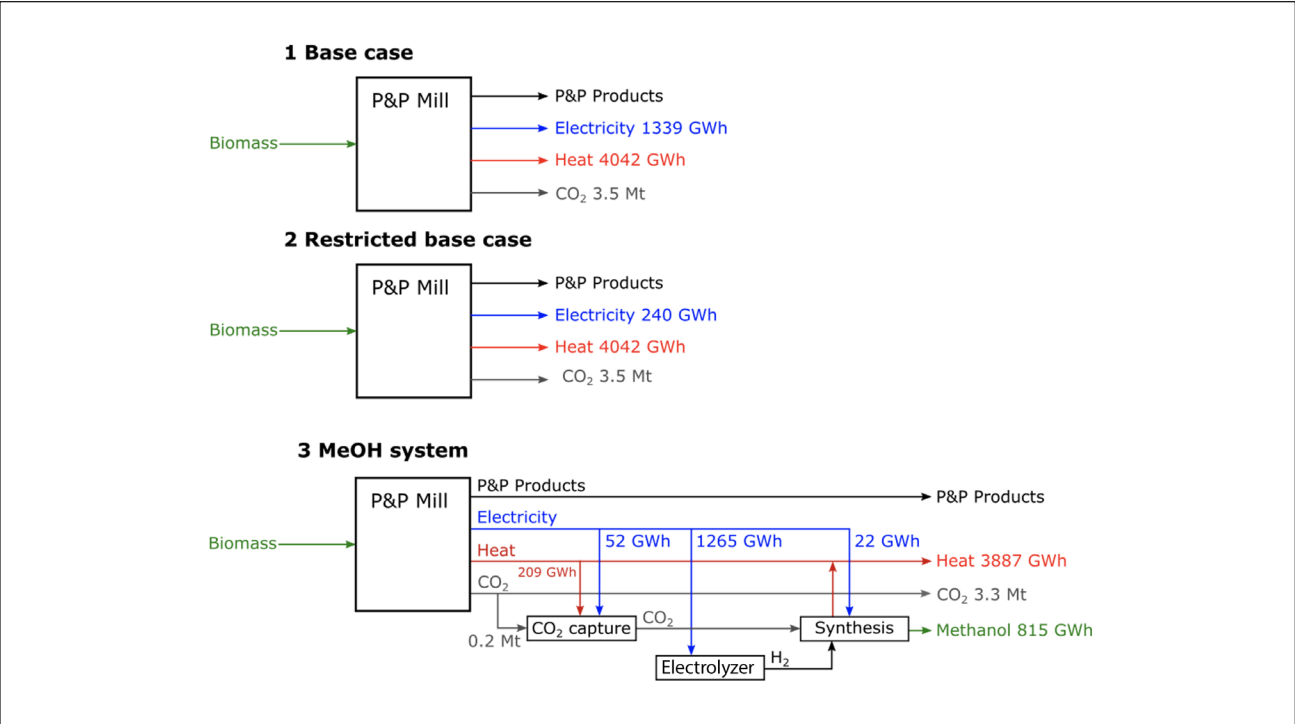
RESULTS AND DISCUSSION

Energy flows for case 1 (base case) are rather simple, as all heat and electricity that are not required by the pulping process are sold to the grid. Case 2 (restricted base case) is

otherwise identical but the electricity sales are restricted. For the methanol case, the electrolyzer produces a significant amount of heat, albeit at a low temperature (70°C–80°C). This heat is assumed to have no value in this study, although modern heat pumps could be used to prime the heat to suitable applications.

Synthesis heat is assumed to be usable in the CO₂ capture, which reduces the outtake from the pulp mill side. Overall, the demand of heat in the CO₂ capture is rather low compared to the total heat output of the mill.

Available electricity forms the bottleneck for methanol production. Energy and CO₂ flows for cases 1–3 are illustrated in **Fig. 5**. The corresponding flows for case 4 (hybrid) are not depicted, but they would lie somewhere between case 1 and case 3, depending on the ratio of electricity sold to grid-to-consumption in methanol production.



5. Simplified energy and material flows for cases 1-3 (MeOH = methanol).

Profitability

Two critical limits for the profitability can be identified. The first one is achieved when the additional income from the fuel sales exceeds the capital and operational expenses associated with fuel production. It is debatable whether the electricity and heat costs should be included in these expenses or not. The second profitability limit is reached when, in addition to the first condition, the total income exceeds that of the base case, where profits are made simply by selling the pulp mill's excess electricity and heat. This is referred to as *superior profitability* in the context of this work.

With 8000 full load hours, capital and operational expenses (excluding electricity and heat cost) in the methanol (MeOH) case amount to 52.4 €/MWh_{MeOH}. About 75% of these costs are associated with fixed equipment cost and 25% with operating costs. If the market price of methanol were to be 400 €/metric ton (62.6 €/MWh_{MeOH}), there would still be a profit margin of 10.2 €/MWh_{MeOH} after subtracting the production expenses (again, excluding electricity and heat). If the cost associated with heat is ignored, the average internal cost of electricity would then have to be below 6.6 €/MWh, which accounts also for the stoichiometric losses in the process. This represents the *limit price* necessary for electricity to reach the first profitability limit that was defined earlier.

The limit price of electricity is dependent on the assumed parameters, with the prices of methanol and heat having a substantial impact, as well as the assumed equipment costs and efficiencies. The sensitivity of limit price to

Price of MeOH,		Limit Price of Electricity, €/MWh
€/ton	€/MWh	
200	31.3	-
300	46.9	-
400	62.6	6.6
500	78.2	16.7
600	93.9	26.7
700	109.5	36.8
800	125.2	46.9

IV. Calculated limit price of electricity that corresponds to different methanol (MeOH) market prices.

methanol price is shown in **Table IV**. For reference, the average annual electricity price in the European power exchange (EPEX) spot market in the German-Luxemburg area in 2019 was 37.7 €/MWh. Thus, a premium of nearly 300 €/ton (1.75-fold increase) would be necessary if the fossil methanol price is 400 €/ton.

The electrolyzer also produced oxygen, as was mentioned in the "Electrolysis" section. Using a very conservative price for oxygen of 15 €/metric ton [54], annual savings of about 0.7 M€ could be obtained at a 1.5 M a.d. metric ton mill that uses 30 kgO₂/a.d. metric ton. This does not cause a significant change in profitability, as its impact is low compared to other expenses (**Table V**).

Case Number		1 Base Case	2 Restricted Base Case	3 MeOH Case
Additional Expenses				
Synthesis capital expense	M€/year			10.3
Synthesis operational expense	M€/year			3.3
Electrolyzer capital expense	M€/year			14.5
Electrolyzer operational expense	M€/year			2.8
CO ₂ capture capital expense	M€/year			2.3
CO ₂ capture operational expense	M€/year			8.6
Total	M€/year	0	0	41.8
Income				
Heat	M€/year	40.4	40.4	38.9
Electricity	M€/year	40.2	7.2	0
Methanol	M€/year	0	0	51.0
Total	M€/year	80.6	47.6	89.9

V. Expense and income distribution of the reference and methanol (MeOH) cases.

The conditions necessary for reaching superior profitability with the methanol case are presented in **Fig. 6**. With reasonable electricity prices (20–40 €/MWh), the methanol price would have to be around 600–800 €/metric ton. However, if the electricity sales are limited, for instance due to an undeveloped grid, superior profitability can be reached with much lower methanol prices. Thus, in locations where grid improvements are necessary, it could be worthwhile to investigate PtX integration options as one potential alternative for increasing revenue and profit.

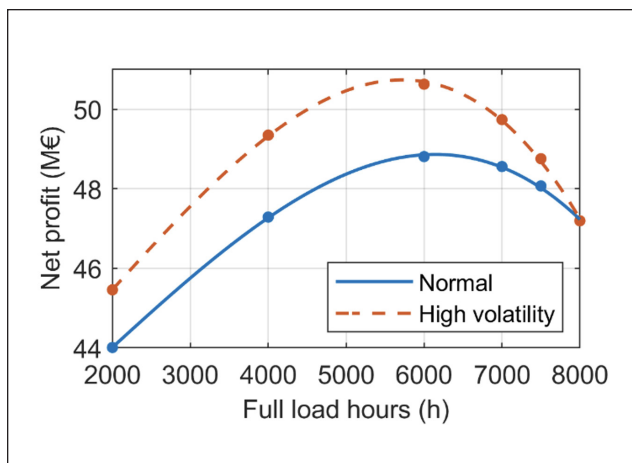
A methanation plant could also operate based on the electricity price; selling electricity when its price is high and converting electricity directly to methanol when the market price is low. While this decreases the running costs of the plant, it also increases the pressure from capital expendi-

tures. Furthermore, the dynamic control of chemical processes can be difficult, potentially requiring additional buffer storages. A study [65] has concluded that it is better to maximize the capacity ratio, even if it results in a minor increase in running costs. The simulations performed in this study showed that hybrid operation was slightly superior to baseload operation (3.4% increase in annual net profit), but this result is affected by a few factors:

- It was assumed that the PtX plant operates at the lowest electricity prices and sells electricity during the peak price hours. In reality, there could be hourly fluctuations that are too rapid for the plant to follow, or otherwise unattainable due to technical reasons.
- Shutdowns and restarts of the plant were not simulated.

		a							b				
Methanol price (€/ton)		Electricity price (€/MWh)					Methanol price (€/ton)		Electricity price (€/MWh)				
		0	20	40	60	80			0	20	40	60	80
200		-18.7	-45.5	-72.3	-99.1	-125.9	200		-18.7	-23.5	-28.3	-33.1	-37.9
400		6.8	-20.0	-46.8	-73.6	-100.3	400		6.8	2.0	-2.8	-7.6	-12.4
600		32.3	5.5	-21.3	-48.1	-74.8	600		32.3	27.5	22.7	17.9	13.1
800		57.8	31.0	4.2	-22.5	-49.3	800		57.8	53.0	48.2	43.4	38.6
1000		83.3	56.5	29.7	3.0	-23.8	1000		83.3	78.5	73.7	68.9	64.1

6. Profit of MeOH case (in M€/year) compared to base case (a) and restricted base case (b), where electricity sales are limited to 30 MW.

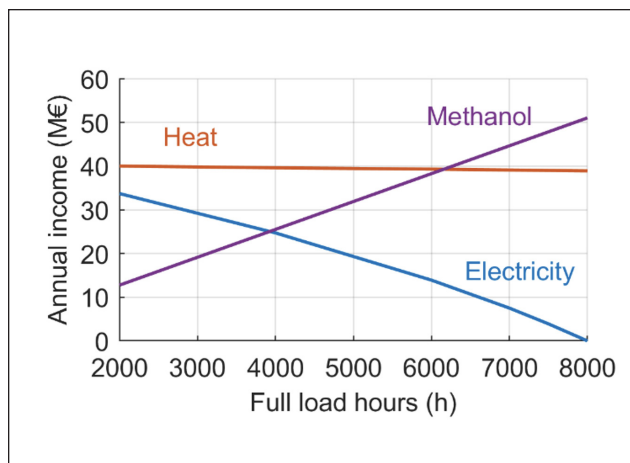


7. Net profit of hybrid case as a function of full load hours under normal electricity price scenario and high volatility scenario (50% price fluctuations with identical annual average price).

- No additional costs were associated with buffer storages or other upgrades that would be necessary for hybrid operation.
- The results were calculated using the hourly Elspot electricity market data for Finland in 2019. Different markets could give different outcomes.

A significant increase in volatility of the electricity price could strengthen the profitability of the hybrid operation mode even more, as seen in **Fig. 7**. Assuming that the electricity price fluctuation increases by 50% while the annual average remains unchanged, the annual profits would increase by 3.8%. Cost distribution from the various income items is shown in **Fig. 8**. The relative price difference between electricity and methanol is the enabling factor for hybrid operation.

The studied scenario is specifically designed for a modern pulp mill utilizing biomass extensively as the feedstock. This configuration resulted in the production of excess electricity, which is not a guaranteed outcome for all types of mill configurations in other locations. However, both the studied mill and other configurations could potentially use externally produced electricity, for instance by using wind turbines or solar photovoltaics. Thus, the proposed study is not strictly limited to only mills with excess electricity. Still, the price at which this external electricity would be available largely determines the profitability of the proposed synthesis integration. This study compares the opportunity cost of not directly selling excess electricity from the mill but instead using it to yield additional products. The incentive for this activity is fundamentally derived from the price difference between the electricity sales and synthesized products. Fundamentally, the situation remains the same even if external electricity production would be used, albeit the additional cost of procuring that electricity would need to be accounted for both the reference case and the e-fuel case.



8. Distribution of the annual income items in hybrid operation with varying full load hours.

From an environmental point of view, an individual operator of an electricity producing facility can pose the question whether the greatest environmental benefit is gained by selling low-emission electricity to the grid or by using that electricity to produce low-emission products. In the context of this paper, a pulp mill could choose to sell excess electricity to the grid or, for instance, convert the electricity to hydrogen and subsequently produce methanol. The marginal effect in electricity market would be that some operator, possibly using fossil resources, would be taking the place in the market previously covered by the pulp mill. The environmental benefit is measured as the reduction of the emission intensity of grid electricity sold on the market. Simultaneously, the pulp mill would become a new supplier of methanol, which could potentially replace the demand of some conventional fossil methanol. Which of these alternatives is environmentally a better alternative could be investigated in future works for different regions and products in a more precise manner.

CONCLUSIONS

Selling e-methanol instead of electricity could be profitable in pulp mills if the methanol price is at 600–800 €/metric ton and the average annual electricity price is 20–40 €/MWh. As the fossil methanol prices have been ranging between 300–500 €/metric ton during recent years, such mill configurations could be considered feasible even today if suitable premiums for renewable methanol are available. Moreover, the competitiveness of methanol-integrated pulp mills would be even greater if there are limitations to the amount of electricity that could be sold to the grid without significant capacity-upgrading investments. Given that many currently planned and proposed pulp and paper mill projects are located in rural and remote regions of the world, Power-to-X systems should be considered among other alternatives as a potential tool for managing excess electricity in pulp mills and creating additional revenue.

Available electricity forms a bottleneck for a power-to-methanol configuration. Heat and CO₂ flows of the mill are barely affected by the introduction of methanol production, unless additional electricity sources are incorporated into the plant. Methanol synthesis and hydrogen production by electrolyzers can produce a significant quantity of low-temperature heat, as well as oxygen for use in the mill. With appropriate design, the electrolyzer could cover the whole oxygen demand of the mill. First, smaller demonstration projects could aim to maximize the utilization of oxygen as a side product, providing valuable experience that could later be beneficial in utilizing oxy-combustion, for instance.

Flexible operation of the synthesis plant according to electricity price could potentially provide additional profit when performed in moderation, but a more thorough analysis is required for verification. Increased volatility in electricity prices could further enhance the potential benefits from flexible operation. Integration of power-to-X schemes with pulp mills offers numerous possibilities for increasing flexibility and self-sufficiency, for instance by allowing adjustable operation between export products and internal use of electricity, heat, and chemicals.

The optimal dimensioning of the plant is something that should be explored in further studies. Efficient utilization of byproducts, like oxygen, could prove to be a good early demonstration opportunity. Electrolyzers that would consume only a portion of the available electricity could increase the flexibility tools available for the plant. Furthermore, the environmental impact of the methanol product and its impact on global or regional emission could be explored in further works. This could give an indication on how the pulp and paper sector could best serve to reduce emissions, whether it occurs through the electricity market or through fuel and chemical production. In the next stage of research, the different flue stacks and sources of CO₂ from the pulp mill should also be compared in terms of applicability and cost, while also accounting for the different alternative application scales. **TJ**

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ABOUT THE AUTHORS

The topic of this research is quite relevant right now, and few existing papers have acknowledged the potential and possibility of this kind of system integration. The field also supported our research strengths. This paper combines research from two sub-genres, the pulp and paper sector and power-to-X sector, which have not been extensively studied before.

The most difficult aspect of this research was data management and version control of the simulations. We solved this issue by streamlining calculations and proper documentation.

Through this study, we discovered the usefulness of durability curves in estimations involving variable prices and their annual impact. Our findings shed

some light on the energy and material volumes, which are surprisingly high/low, depending from which viewpoint the results are interpreted.

For mills, this study provides fresh ideas and food for thought relating to mill product portfolios and flexibility. A next step could be the linking of externally sourced electricity into the processes of mills.

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