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Multi-time integration approach for combined pulp and ammonia production and seasonal CO_2 management

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ABSTRACT

In this work, the gasification of the black liquor is proposed as an alternative ammonia production route. Due to the seasonal variation of the energy prices, a multi-time integration approach that combines different technologies and energy inputs is used to identify the most suitable operating conditions and arrangements that minimize the energy resources consumption. As a result, the integration of technologies such as power-to-gas systems, carbon capture and injection units, along with liquid fuel storage, may help offsetting the intermittency of the renewable energy resources and increasing the economic revenues of the integrated pulp and ammonia plant. The optimal CO_2 management and synthetic natural gas storage may ensure a reliable operation even during the strained periods of the electricity grid. Also, the credits obtained from the injection of biogenic CO_2 emissions may compensate for the investment cost associated to the implementation of these new technologies.

1. Introduction

Due to increasing concerns about the environmental impact of the production of power, fuels and chemicals, many efforts are put to come up with alternatives to attend these demands in more sustainable ways. However, the adopted approaches must deal not only with the mitigation of emissions, but also take into account the uncertainties about the prices of the energy supplies and the carbon taxes likely adopted in future scenarios of more severe environmental regulations (Florez-Orrego et al., 2022). Also, rigorous process synthesis and economic analysis are crucial for the decision making of the best pathways to boost bioeconomy (Ribeiro Domingos et al., 2023). As a well-stablished biomass-based industry and a relevant economic activity, the pulp and paper industry can play an important role in the decarbonization process. In fact, this industry is considered one of the largest energy consumers in the industrial sector (IEA, 2020), accounting for 5.3% of worldwide industrial energy consumption in 2020 (IEA and EPE, 2022). Despite the fact that up to 30% of the total energy use in pulp mills is provided by the produced black liquor (BL), some fossil fuels are still used for onsite utilities supply. Decarbonizing those utilities by switching to low-carbon fuels has a significant impact on the carbon footprint of this industry (IEA, 2020).

On the other hand, ammonia is one of the most demanded bulk chemicals in the world, mainly for the production of fertilizers for the agricultural sector (Florez-Orrego et al, 2023a). In 2016, the ammonia production reached 175 million tons, and the trend from 2006 to 2016 shows a growth rate of 1.9% per year (YARA, 2018). Ammonia production accounts for around 2% of the total final energy consumption and 1.3% of CO_2 emissions from industry, as it is heavily based on fossil fuels (IEA, 2021). Pre-combustion CO_2 capture is an inherent part of the ammonia production process, and the CO_2 rich-stream coming from the syngas purification may be reused or permanently stored. In 2020, about 130 Mt of CO_2 were used to produce urea, whereas only 2 Mt of CO_2 were stored (IEA, 2021). The way in which the electricity consumed is generated also influences the CO_2 emissions of the Haber-Bosch process. The indirect CO_2 emissions related to the electricity import accounted for 40 Mt of CO_2 in 2020 (IEA, 2021). Thus, several efforts have been made towards the mitigation of the environmental impacts of fertilizers sector. The nitric acid and urea production has been analyzed in terms of thermodynamic, environmental and economic indicators aiming to reduce the environmental burden and improve the CO_2 management

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Nomenclature

Latin symbols

b	specific chemical exergy (kJ/kg)
B	chemical exergy (kW)
C_0, C_1	cost at the reference scale (EUR)
f	unit load optimization factor (-)
m	mass flow rate (kg/h)
N	number of utility units, temperature intervals, yearly periods (-)
$N_{hours\ per\ year}$	number of operative hours per year (h)
q	cooling or heating duty from the utility systems (kW)
R	cascaded heat rate (kW)
S_0	reference scale capacity (various)
S_1	actual scale capacity (various)
T	temperature (°C)
W	electrical power (kW)
y	binary (existence) optimization factor (-)
Z_{equip}	investment cost (Eur)

Greek symbols

ω	utility or process unit

Abbreviation

AF	annualization factor
BL	black liquor
BLG	black liquor gasification
CAPEX	capital expenditure (Eur)
CW	cooling water
LHV	lower heating value (kJ/kg)
MER	minimum energy requirement (kW)
MVR	mechanical vapor recompression
OPEX	operating costs (Eur)

Subscripts

AD	air dried
Dest.	destroyed
exp.	exported
imp.	imported
r	interval of temperature

utilization (Ribeiro Domingos et al., 2022). The biomass thermochemical conversion routes for syngas production are among the options to supply feedstock and energy to the ammonia plants, especially in countries with a long biomass conversion expertise (Telini et al., 2022). Other authors analyzed the production of hydrogen and ammonia using different residual biomass, including orange and sugar cane bagasse, as well as sewage sludge, looking to decarbonize the fertilizers and industrial sectors traditionally dependent on those bulk chemicals (Vargas et al., 2022). Other pathways suggested reusing CO_2 for the production of different chemicals and fuels aiming to increase overall process efficiency (Peter, 2018). The power-to-gas approach is based on water electrolysis for hydrogen production, which combined with CO_2 produces synthetic natural gas via methanation process. This technology is pertinent for CO_2 and energy management purposes, as methane can be produced during periods of inexpensive electricity generation and stored to be used in due time when the energy import is more expensive (Florez-Orrego et al., 2022).

Castellani et al. assessed the potential of using N_2/CO_2 membrane separation of flue gas and water electrolysis to produce ammonia through the Haber-Bosch process and methane via the Sabatier reaction. The authors found that the electrolysis is responsible for 80% of the energy costs and the CO_2 recycling process is subject to the availability of renewable electricity in order to avoid net emissions (Castellani et al., 2018). Vandewalle et al. studied the effects of integrating the power-to-gas approach on the power, gas and carbon sectors. This technology directly impacts the final gas price, since it increases the capacity and flexibility of the system, and contributes to enhancing the sustainability of the process (Vandewalle et al., 2015). The power-to-gas approach may reduce the need for permanent CO_2 storage, but not the need of short-term storage, since it is necessary to maintain the operation of the system, which may lead to a complex CO_2 network. Other authors also showed that the integration of the power-to-gas technology in the natural gas and electric grids may reduce the total energy loss and maintain a stable operation level (Zeng et al., 2016). However, the capture and management of the carbon dioxide derived from an integrated pulp and ammonia production plant has not been assessed, neither it has been studied the decarbonization potential on scenarios of carbon taxation and variable energy input prices.

For this reason, the aim of this paper is to apply a systematic approach to the analysis of a multi-time problem that considers seasonal energy costs, CO_2 capture technologies, storage systems and power-to-gas to decarbonize the ammonia production and offset the shortcomings of the renewable energy systems, as electricity can be stored or consumed, depending on the variable electricity prices. This approach ensures that renewable energy can be used efficiently and cost-effectively, even when the production levels vary over time. In addition, the proposed CO_2 management system synergistically integrate advanced technologies, which can significantly contribute to mitigate the carbon footprint of industrial processes. Thus, differently from previous studies, the novelty of this works relies on the integration of two chemical plants in order to (*i*) capitalize on the residues of the former; (*ii*) manage CO_2 emission as a means for storing intermittent renewable energy; (*iii*) decarbonize the ammonia and pulp sectors by substituting fossil fuel consumption by renewable energy resources; and (*iv*) determine the additional capital expenditure associated to the incremental costs of the new integrated facilities.

3. Methods and tools

In this section, the modeling and simulation methods and tools, as well as the optimization problem definition subject to minimum energy requirements, considering carbon taxation and seasonal energy cost variation, are presented. The key performance indicators to evaluate the two cases are also described in this section. A comparative analysis of two case studies is proposed:

Case (1) an integrated pulp and ammonia production plant using black liquor gasification, with typical utility systems (e.g. chips, bark and oil furnaces; steam network; electricity import or export);

Case (2) an integrated pulp and ammonia production plant using black liquor gasification, with its respective utility systems, and CO_2 management systems, namely post-combustion CO_2 capture, liquefaction, storage and injection units; and methanation, synthetic natural gas (SNG) liquefaction and storage units. An electrolysis system is also integrated to convert surplus available electricity and water during the summer season into hydrogen and heat.

2.1. *Process modeling and simulation*

Fig. 1 shows the process flowsheet of the kraft pulp mill, wherein cellulose is extracted from wood under strong alkaline conditions. Around 10% of the biomass input that is lost in log debarking, chipping and chips classification is used in the biomass boiler as fuel. In a standalone pulping mill, the weak black liquor follows to a recovery unit, where it is concentrated in multiple-effect evaporators and burned

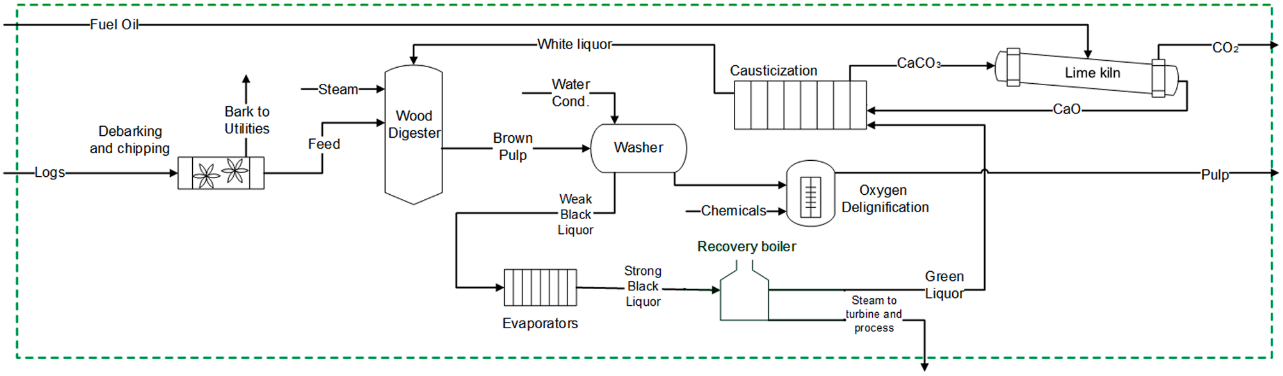

Fig. 1. Process flowsheet of pulp production mill.

in the recovery boiler to generate power and steam. The green liquor produced during the combustion of the strong black liquor is treated in the causticization process, producing the white liquor that can be recycled back to the wood digester. Although the steam produced in the recovery boiler accounts for most of the steam consumption in the pulp mill, the balance must be still supplied using bark and importing additional wood chips (Moraes, 2011). Fuel oil or fossil natural gas is also widely used in the lime kilns of the causticization process, but they could be substituted by more environmentally friendly energy inputs, as it will be discussed further in this work. The pulp yield is 46.51% wt. of the total amount of digested biomass, whereas black liquor production rate is 1.44 t_{BL}/t_{pulp} (Foelkel, 2017). Power and steam demands are adapted for a pulp production of 877.83 t_{ADPulp}/d (Ferreira and Balestieri, 2015; Moraes, 2011).

In contrast, Fig. 2 depicts the integrated proposed approach, in which the black liquor is gasified instead of burned, in order to produce value-added syngas and waste heat. In the syngas production unit, the weak black liquor is firstly dried in a mechanical vapor recompression system that only consumed electricity. Subsequently, the strong black liquor is gasified in a pressurized entrained flow reactor using oxygen (30 bar, 1,000 °C), allowing to recover as smelt the chemicals that are recycled back as green liquor to the causticization process and then to the digester. Next, the syngas obtained needs to be treated, purified and its composition must be adjusted before it enters to the ammonia loop (Florez-Orrego and Oliveira Jr, 2017). To this end, an auto-thermal reformer, a water gas shift, a CO_2 capture and a methanation systems are required. Finally, ammonia is produced in an intercooled catalyst bed, before it is chilled and separated for export (cf. Fig. 2). The entire process is modeled in Aspen Plus® v.8.8 software and the detailed description of the processes conditions is reported in (Domingos et al., 2021b). The Peng-Robinson equation of state with Boston-Mathias modifications (PR-BM), recommended for nonpolar or mildly polar mixtures, gas-processing and refinery is used (Aspentech, 2011). In addition, the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) is used to model the physical absorption of CO_2 with dimethyl ethers of polyethylene glycols (DEPG) as suggested in (Flórez-Orrego et al., 2020).

For the CO_2 management, a set of options is defined. The CO_2 captured in the syngas purification unit could be dried, compressed and injected into a gas reservoir. It can be also liquefied and stored in a tank at -50 °C and 7 bar (1,155 kg/m^3). Liquefied CO_2 can be later regasified and fed to a methanation system, in which the hydrogen necessary is provided by a water electrolyzer with a specific electricity consumption of 55 kWh/kg_{H2} (JPI Urban Europe, 2019). The methanation system is based on the TREMP® process (Topsøe, 2009), in which a series of methanation beds are intercooled either by recycling or indirect intercooling in order to achieve higher reactants conversion (Nakashima et al., 2023). The produced CH_4 is liquefied, stored at -162 °C and 1 bar (423 kg/m^3), and it can be later used in the synthetic natural gas burner to substitute the consumption of fuel oil in the lime kiln of the kraft pulp mill. Apart from the CO_2 stream leaving the syngas purification unit of the ammonia plant, another important CO_2 stream is the one present in the flue gas coming from the furnaces. This CO_2 can be captured in a CO_2 post-combustion system using chemical absorption solvent (Flórez-Orrego et al., 2020), at the expense of an specific steam consumption of 3.6 MJ/kg_{CO2} with a capture efficiency of 90% (Florez-Orrego et al, 2023b). Next, the purified CO_2 follows to the dryer and compression system either to be stored or injected.

The furnace models (i.e. wood, oil, synthetic natural gas, bark, black liquor) consider the thermophysical properties of the fuels (e.g. stoichiometric molar air to fuel ratio, lower heating values, equivalence ratio, minimum flue stack temperature, air preheating temperature, and heat loss). Meanwhile, the cooling tower assumes supply and return temperatures of 12 °C and 40 °C, respectively, with a consumption of electricity of 0.021 kW_{el}/kW_{th} per unit of cooling duty (Couper et al., 2012).

2.2. Optimization problem definition

The introduction of the new energy technologies shown in Fig. 2 in a traditional kraft pulp mill entails the redefinition of the complete energy balance and calls for a systematic method and computational tool to perform the complex energy integration and optimization problem.

The solution is handled by OSMOSE Lua platform Florez-Orrego et al., 2022), which first determines the minimum energy requirement (MER) of the chemical plants (i.e. integrated pulp and ammonia production plant, see green area of Fig. 2). The MER is calculated by considering the individual contributions of the hot and cold streams to the overall heat balance. This is achieved by combining them into their respective hot and cold composite curves, with a minimum temperature approach (ΔT_{min}) being imposed as a physical constraint. The ΔT_{min} ensures that these composite curves are shifted apart from each other, thus allowing for reasonable heat transfer rates. The specific value of ΔT_{min} depends on the nature of the stream, with gas, liquid, and two-phase streams assuming values of 8 °C, 5 °C, and 2 °C, respectively. The Eqs. (1-(3) outline the optimization problem necessary to determine the MER.

$$\min_{R_r} R_{N_r+1} \tag{1}$$

Subject to:

Heat balance of each interval of temperature r:

$$\sum_{i=1}^{N} Q_{i,r} + R_{r+1} - R_r = 0 \quad \forall r = 1..N \tag{2}$$

Feasibility of the solution:

$$R_r \geq 0 \tag{3}$$

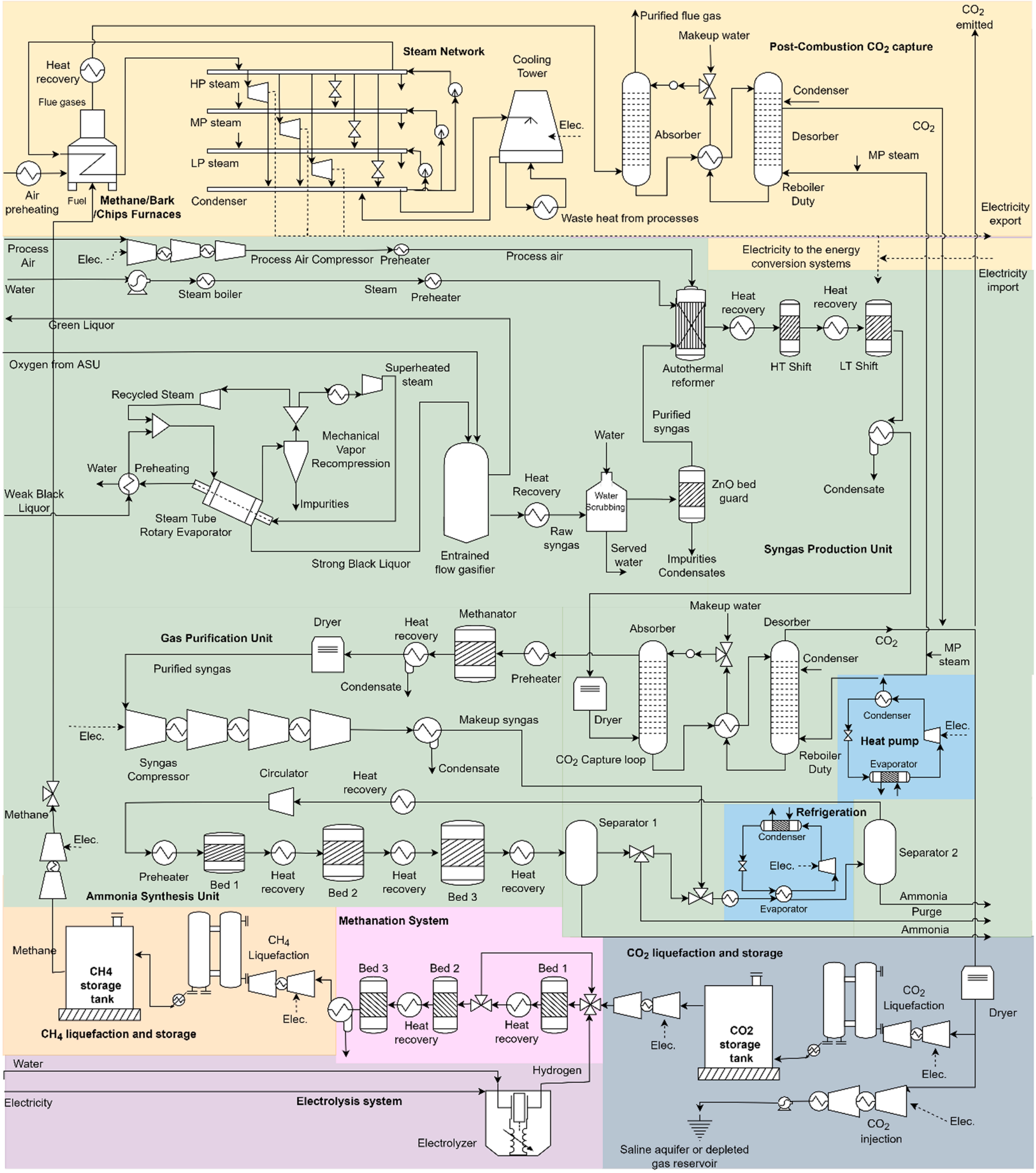

Fig. 2. Superstructure for the integrated pulp and ammonia production process via black liquor gasification including the utility system, with post-combustion CO_2 capture, power-to-gas appliances, liquids storage and injection units.

where:

N is the number of temperature intervals defined by considering the supply and the target temperatures of the entire set of streams;

Q is the heat rate exchanged between the process streams ($Q_{i,r} > 0$ for hot stream, $Q_{i,r} < 0$ for cold stream);

R is the heat rate cascaded from higher ($r + 1$) to lower (r) temperature intervals (kW);

Next, the computational framework finds the most appropriate utility systems and their respective operating conditions that lead to the lowest resources consumption and optimal operating cost Flórez-Orrego et al., 2020). Data transfer between OSMOSE and ASPEN Plus® software is also automatically managed. The mixed integer linear programming (MILP) problem described in Eqs. (4-(8) minimizes the objective function, Eq. (4), and determines the binary variables y_w related to the selection of a given utility unit ω, and its corresponding continuous load factor, f_w, as well as the investment cost associated to the implementation of these technologies. In other words, this optimization problem minimizes the resources consumption (wood chips, oil, and electricity) and, thus, minimizes the operating cost of the chemical plant. The investment required to purchase these new technologies (capital expenditure or capex) is also minimized, while satisfying the described constraints. In summary, the optimization problem accounts for the trade-off between buying the new technologies and affording the operating costs and revenues that are associated to a certain operating scenario.

$$\min_{\substack{f_\omega,\ y_\omega \\ R_r, W}} \left[\begin{array}{l} f_{chips} \times (B{\cdot}c)_{chips} + f_{wood} \times (B{\cdot}c)_{wood} + f_{oil} \times (B{\cdot}c)_{oil} \pm f_{\frac{power}{grid}} \times (W{\cdot}c)_{\frac{power}{grid}} \\ + f_{envEm} \times (m{\cdot}tax)_{envEm} + f_{water} \times (B{\cdot}c)_{water} + \dfrac{Z_{equip} * AF}{N_{hours\,per\,year}} \\ - f_{pulp} \times (B{\cdot}c)_{pulp} - f_{NH_3} \times (B{\cdot}c)_{NH_3} - f_{\frac{CO_2 market}{or\ injected}} \times (m{\cdot}c)_{\frac{CO_2 market}{or\ injected}} \end{array} \right] \tag{4}$$

Subject to:

Heat balance at the temperature interval *(r):*

$$\sum_{\omega=1}^{N_\omega} f_\omega q_{\omega,r} + \sum_{i=1}^{N} Q_{i,r} + R_{r+1} - R_r = 0 \quad \forall r = 1..N \tag{5}$$

Balance of produced/consumed power:

$$\sum_{\omega=1}^{N_\omega} f_\omega W_\omega + \sum_{\substack{chemical \\ units}} W_{net} + W_{imp} - W_{\exp} = 0 \tag{6}$$

Existence and size of the utility unit:

$$f_{\min,\omega} y_\omega \le f_\omega \le f_{\max,\omega} y_\omega \quad \forall \omega = 1..N_\omega \tag{7}$$

Feasibility of the solution (MER):

$$R_1 = 0,\ \ R_{N+1} = 0,\ \ R_r \ge 0 \text{ and } W_{imp} \ge 0,\ \ W_{\exp} \ge 0 \tag{8}$$

where:

N_w is the number of units in the set of utility systems;

B is the exergy flow rate (kW) of the resources entering or leaving the integrated energy system;

c stands for the buying costs (Eur per kWh, m^3 or kg) of the biomass feedstock and the electricity consumed, along with the CO_2 taxation, as well as for the selling price of the marketable pulp and ammonia (main products), and also the surplus power exported and the CO_2 produced, sold or injected by the integrated energy system;

q is the heating/cooling flow rates supplied by the selected utility systems (kW);

W is the power produced by either the utility systems (i.e. steam network) or the chemical processes (e.g. expanders); or imported from/exported to the grid (kW);

AF is the annualization factor;

$N_{hours\ per\ year}$ is the number of operative hours per year (8760 h);

Z_{equip} is the investment cost (Eur) (cf. Section 2.3.3).

The utility units are modeled via equation-oriented subroutines (Yoo et al., 2015), which requires additional equations for mass and energy balances for water, biomass, syngas, ammonia, pulp, methane, carbon dioxide, power, and heat flows between units. The steam network is responsible for recovering the waste heat produced in the chemical plant, which directly impacts the fuel import. The optimal steam levels are determined by examining the grand composite curve of the chemical process. The choice of importing electricity from the grid or purchasing additional fuel will depend on the performance of the cogeneration systems, and also on the respective cost associated to the electricity and wood chips. This decision is a result of the operating cost optimization problem, and it is handled by the OSMOSE platform.

The market prices of the feedstock and the products considered are summarized in Table 1. The carbon tax for fossil emissions and the credits for biogenic CO_2 injection are both set as 100 Eur/t_{CO2}, in agreement with the scenario of Net Zero Emissions by 2050 (IEA, 2021).

According to Table 2, cheap electricity prices are considered during the period of March-October, as distributed electricity generation by prosumers is higher, whereas more expensive electricity prices are considered during November-February period (dunkelflaute). This assumption allows to simulate not only the seasonal energy costs of intermittent and renewable energy resources, but also to elucidate the factors that affect the energy and CO_2 management of the integrated pulp and ammonia production system in the integrated case study. In other words, the optimization routine must work out the best configurations for CO_2 management when capture, storing, injection or power-to-gas approaches for fuel production are adopted.

Eqs. (9) and (10) are the balance equations for the amount of liquefied gas stored in the tanks, being that the continuous variable f_{tank} accounts for the optimization variable of the tank capacity, and the mass or energy coming in or out the storage systems depend on the operating capacities of the energy systems (f), which are also optimized for each time step t.

$$Storage\_\,level_t = f_{\text{tank},t} \tag{9}$$

$$Storage\_\,level_{t+1} - Storage\ \_level_t = MassorEnergy_{IN,\ \ t} - MassorEnergy_{OUT,\ \ t} \tag{10}$$

2.3. Performance indicators

Thermodynamic, economic and environmental aspects are considered to define suitable indicators to evaluate and compare the case studies 1 and 2, as it is described in the next sections.

2.3.1. Exergy efficiencies

Two exergy efficiency definitions are used to compare the studied scenarios. The rational exergy efficiency, Eq. (11), considers that the useful output of the integrated energy systems is the total exergy output (B *in kW*) from the plant, including the surplus CO_2, any purge gas or excess electricity. Although this indicator is a common choice to determine the overall efficiency of complex energy systems, it overestimates the actual efficiency as it assigns value to residual exergy that otherwise could have been rather converted into more of one of the two main products (ammonia and pulp).

$$\eta_{\text{Rational}} = \frac{B_{useful,output}}{B_{input}} = 1 - \frac{B_{Dest}}{B_{input}} = 1 - \frac{B_{Dest}}{B_{oil/natural\ gas} + B_{wood} + B_{chips} + W_{net}} \tag{11}$$

On the other hand, the relative exergy efficiency, Eq. (12), quantifies the deviation from the minimum theoretical exergy consumption necessary to make up the main chemical products, i.e. pulp and ammonia:

$$\eta_{\text{Relative}} = \frac{B_{consumed,\ ideal}}{B_{consumed,\ actual}} = \frac{B_{ammonia} + B_{pulp}}{B_{oil/natural\ gas} + B_{wood} + B_{chips} + W_{net}} \tag{12}$$

In both Eqs. (11) and (12), the total exergy input is the sum of all the

Table 1
Market costs and selling prices for feedstock and products.

	Market cost/selling price	Reference
Wood	0.013 Eur/kWh	(Trading Economics, 2022)
Chips	0.016 Eur/kWh	(Trading Economics, 2022)
Oil	0.018 Eur/kWh	(Statistics Austria, 2018)
Pulp	0.144 Eur/kWh	(Celulose online, 2018)
Ammonia	0.098 Eur/kWh	(Flórez-Orrego et al., 2019)
CO_2 exported	0.0084 Eur/kg	(Florez-Orrego et al., 2017)

Table 2
Monthly electricity costs assumed over the year.

Month	Electricity cost (Eur/kWh)
Jan	0.35
Feb	0.35
Mar	0.001
Apr	0.001
May	0.001
Jun	0.001
Jul	0.001
Aug	0.001
Sep	0.001
Oct	0.001
Nov	0.35
Dec	0.35

energy resources consumed; whereas in Eq. (11), B_{Dest} stands for the exergy destruction, estimated by considering all the subunits of each case study. In order to calculate the exergy efficiency indicators, the specific chemical exergy is assumed as 21.23 MJ/kg_{dry} for wood, 20.13 MJ/kg_{dry} for bark, 12.08 MJ/kg_{dry} for black liquor, 43.38 MJ/kg_{dry} for oil, 19.80 MJ/kg_{dry} for pulp, and for methane (50 MJ/kg_{CH4}) (Domingos et al., 2022a). In addition, the extended exergy analysis takes into account the efficiency of the electricity generation (55.68%), as well as the oil (95.20%) and biomass (86.13%) supply chains, as it has been reported in (Flórez-Orrego et al., 2015, 2014).

2.3.2. CO_2 emissions balance

Both overall and net CO_2 emissions balances are calculated according to Eqs. (13) and (14), respectively. The former balance accounts for the total amount of CO_2 emitted, either from fossil or biogenic sources. Meanwhile, the latter balance considers that the absorption and release of CO_2 during biomass growth and conversion is cyclical, thus the biogenic emission are neglected. Both balances consider the abated emissions in the capture unit as avoided emissions.

$$\begin{aligned}\text{Overall CO}_{2\text{emissions}} = & \text{Oil}^{\text{direct}}_{\text{emissions}} + \text{EE}^{\text{indirect}}_{\text{emissions}} + \text{Wood}^{\text{indirect}}_{\text{emissions}} \\ & + \text{Oil}^{\text{indirect}}_{\text{emissions}} + \text{Biogenic}^{\text{direct}}_{\text{emissions}} - \text{CO}_{2\text{captured}}\end{aligned} \tag{13}$$

$$\text{Net CO}_{2\text{emissions}} = \text{Oil}^{\text{direct}}_{\text{emissions}} + \text{EE}^{\text{indirect}}_{\text{emissions}} + \text{Wood}^{\text{indirect}}_{\text{emissions}} + \text{Oil}^{\text{indirect}}_{\text{emissions}} - \text{CO}_{2\text{captured}} \tag{14}$$

The indirect CO_2 emissions associated with the indirect fossil fuel consumption in the upstream supply chains are assumed, respectively, as 0.0029 and 0.0043 gCO_2 per kJ of oil and wood; whereas 62.09 gCO_2 are indirectly emitted per kWh of electricity consumed (Flórez-Orrego et al., 2015).

2.3.3. Calculation of investment costs

Eq. (15) is used to estimate the capital expenditure (CAPEX) of the main plant equipment, by correlating the actual capacity (S_1) of each unit to a reference capacity (S_0) with known capital cost (C_0). A power scaling factors (r) that varies depending on the type of process is considered (Turton et al., 2018). The correlations and the specific investment cost for the different units are reported in Table 3.

$$C_1 = C_0\left(\frac{S_1}{S_0}\right)^r \tag{15}$$

3. Results and discussion

The results of the optimal processes parameters for case studies 1 and 2 are summarized in Tables 4 and 5, respectively. It must be born in mind that the ammonia and pulp production rates (218.93 t_{NH3}/d and 877.83 t_{Pulp}/d) are fixed for both cases. The power demand of the pulping plant alone attains 2.84 GJ/t_{Pulp}, the black liquor treatment and drying processes consume 1.2 GJ/t_{Pulp}, and the syngas conditioning and ammonia synthesis consume together 0.58 GJ/t_{Pulp} of power (Domingos et al., 2021b).

In case study 1, the extended exergy consumption, which considers the upstream supply chain, is 16–21% higher than the plantwide energy consumption. This value varies between 16 and 25% in the case study 2. The small difference is attributable to the slight increase in energy consumption to drive the additional energy technologies in the case study 2. The power generation of the Rankine cycle is also slightly increased in the case study 2, if compared to the case study 1, especially during the March-October period, in which the monthly power generation is as high as twice that of the remaining months. This behavior is a consequence of the interest in converting surplus CO_2 into synthetic natural gas that will be stored and later used in the seasonal period of higher electricity costs. For this reason, the electricity export is also reduced in the case study 2, aiming to satisfy the internal energy demands, instead of using the waste heat for exporting electricity that could be rather transformed into synthetic natural gas or used to inject more CO_2 to attain a lower emission factor. This fact is in agreement with a strategy of benefiting from the carbon credits derived from the carbon taxed scenarios. In this regard, the amount of CO_2 injected in the case study 2 is for most of the year much larger than the CO_2 vented from the syngas purification unit of the integrated pulp and ammonia production plant of case study 1. The seek for a maximum injection is a result of the CO_2 management of the system, which adopts a radical CO_2 abatement approach at the expense of a higher power consumption in the injection compression battery.

Figs. 3 and 4 show the breakdown of the monthly energy input (i.e. chips, electricity from grid, and oil) for case studies 1 and 2, respectively. As expected, the extent of consumption of each fuel is strongly linked to the seasonal electricity prices defined in Table 2. Interestingly, the fuel oil consumed in case study 1 to fire the lime kiln can be replaced by the synthetic natural gas that has been produced in the power-to-gas system implemented in case study 2. In this way, the new solution adopted in the latter case represents a change of paradigm with respect to the former case, as it allows ruling out the only direct fossil emissions associated to the integrated pulp and ammonia production.

It is also worth noticing an almost invariable consumption of wood chips during the November-February period, mainly as an adaptation to

Table 3
Correlations and specific investment cost for the units.

Unit	Cinv	Attribute	Source
Ammonia from BL gasification plant	$179.9\left(\frac{\dot{m}}{9122}\right)^{0.65}\ [MEur]$	$\dot{m}_{NH3}\ [\mathrm{kg}_{NH3}/\mathrm{h}]$	(Domingos et al., 2022b)
Electrolyzer	$1{,}200\ [Eur/kW]$	$\dot{m}_{electricity}[kW]$	(Birol, 2019)
Post-combustion CO_2 capture	$100{,}000\ [Eur/tpd_{CO2}]$	$\dot{m}_{CO2}[tpd\ of\ CO2\ captured]$	(Flórez-Orrego et al., 2020)
Furnaces	$200\ [Eur/kW]$	$\dot{m}_{fuel\_load}[kW]$	(NERA and AEA, 2009)
Refrigeration	$750\ [Eur/kW_{th}]$	$\dot{m}_{fuel\_load}[kW]$	(Flórez-Orrego et al., 2020)
Cooling tower	$746.749(F_{in})^{0.79}(R)^{0.57}(A)^{-0.9924}(0.022T_{wb}+0.39)^{2.447}\ [Eur]$ [1]		(Panjeshahi and Ataei, 2008)
Methanation	$300\ [Eur/kW_{CH4}]$	$\dot{m}_{CH4}[kW]$	(Baier et al., 2018)

[1] For the cooling water cost estimation: F_{in} is the water flow in t/h, R is the range (°C), A is the approach (°C) and T_{wb} is the wet bulb temperature in °C.

Table 4
Optimal process parameters for case study 1, integrated pulp mill with ammonia production, but without either carbon management or power-to-gas systems.

Process parameter	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Feedstock wood consumption (GJ/t_{Pulp})	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15
Utility chips consumption (GJ/t_{Pulp})	20.72	20.72	0	0	0	0	0	0	0	0	20.72	20.72
Utility electricity consumption (GJ/t_{Pulp})	0	0	4.13	4.13	4.13	4.13	4.13	4.13	4.13	4.13	0	0
Oil consumption (GJ/t_{Pulp})	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05
Overall plant consumption (GJ/t_{Pulp})	62.92	62.92	46.33	46.33	46.33	46.33	46.33	46.33	46.33	46.33	62.92	62.92
Extended plant consumption (GJ/t_{Pulp})	72.93	72.93	56.29	56.29	56.29	56.29	56.29	56.29	56.29	56.29	72.93	72.93
Rankine cycle power generation (GJ/t_{Pulp})	9.13	9.13	1.35	1.35	1.35	1.35	1.35	1.35	1.35	1.35	9.13	9.13
Ancillary power demand (GJ/t_{Pulp})	0.49	0.49	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.49	0.49
Biomass consumption (t_{Wood}/$t_{NH3+Pulp}$)	3.88	3.88	2.58	2.58	2.58	2.58	2.58	2.58	2.58	2.58	3.88	3.88
CO_2 injected (kg/h)	0	0	0	0	0	0	0	0	0	0	0	0
Marketable CO_2 production (kg/h)	50,518	50,518	50,518	50,518	50,518	50,518	50,518	50,518	50,518	50,518	50,518	50,518
Electricity export (kW)	34,405	34,405	0	0	0	0	0	0	0	0	34,405.55	34,405.55

Table 5
Optimal process parameters for case study 2, integrated pulp mill with ammonia production, equipped with carbon management and power-to-gas systems for optimal renewable energy integration.

Process parameter	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Feedstock wood consumption (GJ/t_{Pulp})	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15	41.15
Utility chips consumption (GJ/t_{Pulp})	20.72	20.72	2.64	2.64	2.64	2.64	2.64	2.64	2.64	2.64	20.72	20.72
Utility electricity consumption (GJ/t_{Pulp})	0	0	7.15	7.15	7.15	7.15	4.15	7.15	7.15	7.15	0	0
Oil consumption (GJ/t_{Pulp})	0	0	0	0	0	0	0	0	0	0	0	0
Overall plant consumption (GJ/t_{Pulp})	61.87	61.87	50.93	50.93	50.93	50.93	47.94	50.93	50.93	50.93	61.87	61.87
Extended plant consumption (GJ/t_{Pulp})	71.83	71.83	63.67	63.67	63.67	63.67	58.29	63.67	63.67	63.67	71.83	71.83
Rankine cycle power generation (GJ/t_{Pulp})	9.15	9.15	2.57	2.57	2.57	2.57	2.19	2.57	2.57	2.57	9.15	9.15
Ancillary power demand (GJ/t_{Pulp})	0.49	0.49	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.49	0.49
Biomass consumption (t_{Wood}/$t_{NH3+Pulp}$)	3.88	3.88	2.75	2.75	2.75	2.75	2.75	2.75	2.75	2.75	3.88	3.88
CO_2 injected (kg/h)	46,246	40,416	69,292	69,292	69,292	69,292	59,190	69,292	69,292	69,292	50,518	50,518
Marketable CO_2 production (kg/h)	0	0	0	0	0	0	0	0	0	0	0	0
Electricity export (kW)	28,612	28,682	0	0	0	0	0	0	0	0	28,560	28,560

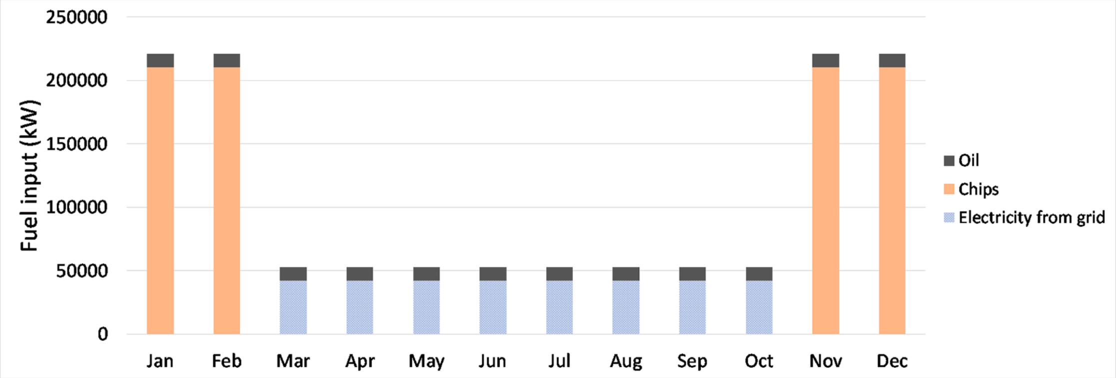

Fig. 3. Breakdown of the monthly fuel and electricity consumption for case study 1. Ammonia and pulp production rates are 218.93 t_{NH3}/d and 877.83 t_{Pulp}/d, respectively.

higher electricity prices and more affordable sources of renewable energy, such as woody biomass. Also, during this period, the synthetic natural gas produced helps reducing the overall energy import, as it can be seen from the monthly variation of methane and carbon dioxide storage, shown in Fig. 5. Advanced energy conversion technologies, such as the carbon abatement units and the liquefied gasses storage, are crucial to ensure a reliable operation of the cogeneration systems, especially when it comes to the reliability of the electrical power supply. In this regard, the CO_2 is recirculated and feed to the methanator only during the months in which the electricity price is low enough, so that it barely impacts the overall economic and environmental performances. According to Fig. 5, stored fuel is preferably used in the months in which the electricity price is high, avoiding a large import of costly electricity from the grid.

Figs. 6 and 7 show the breakdown of the electrical power consumption of the utility systems integrated to the pulp and ammonia production plants for both case studies. In Fig. 6, a relatively low electricity consumption during the March-October period in the first case study (1,000 kW or 1.35 GJ/t_{Pulp}) contrasts with the much higher power consumption during the remainder months of operation (i.e. winter season, 4,500 or 9.13 GJ/t_{Pulp}). The intensive use of the steam network led to an increased amount of pumping and cooling demands, although in lieu of less costly electricity imports.

On the other hand, Fig. 7 shows the breakdown of the electrical power consumption in the case study 2. As expected, an increased number of components in the advanced solution for energy and CO_2 management incurs an increased total power demand. The electrolyzer power consumption is not represented in Fig. 7 for the sake of clarity; but it is activated between March-October period, except for the month of July, during which partial consumption of the stored synthetic natural

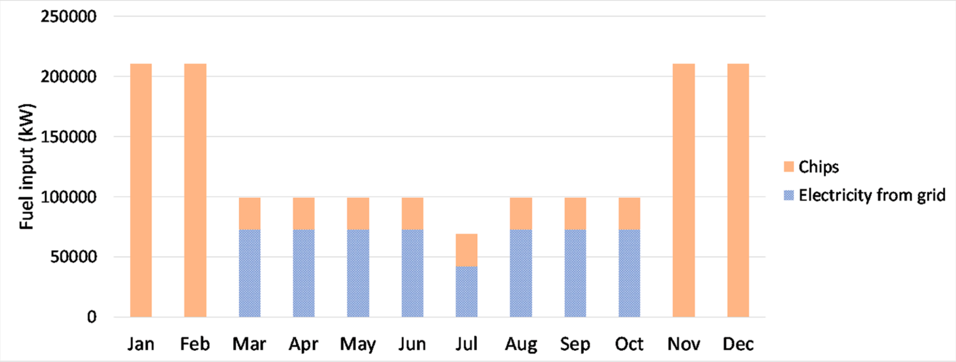

Fig. 4. Breakdown of the monthly fuel and electricity consumption for case study 2. Ammonia and pulp production rates are 218.93 t_{NH3}/d and 877.83 t_{Pulp}/d, respectively.

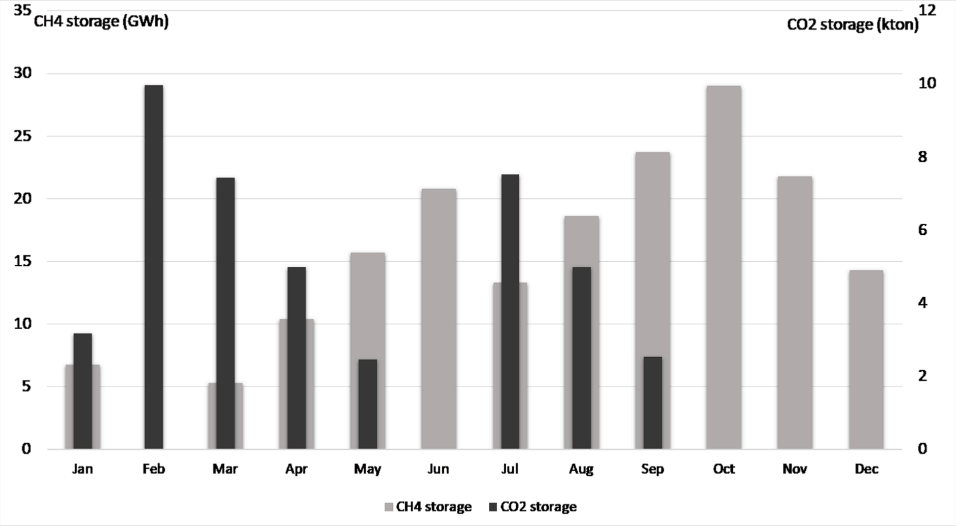

Fig. 5. Monthly variation of methane and carbon dioxide storage for case study 2.

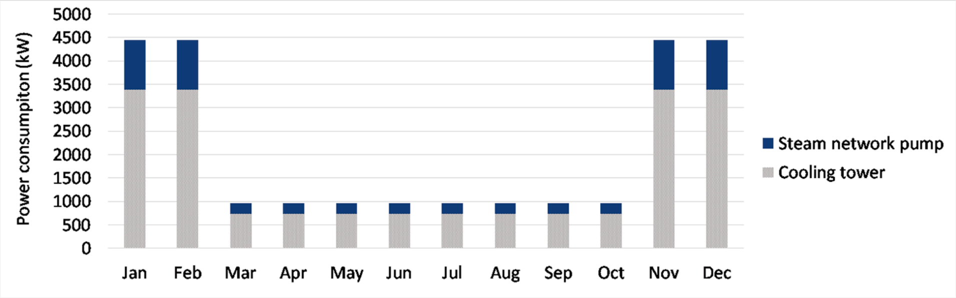

Fig. 6. Breakdown of the monthly electrical power consumption for case study 1.

gas is used to balance the energy consumption. The electricity consumption of the electrolyzer during the active periods is about 34 MW. Regarding the case study 2, larger steam network and cooling units are also necessary to (*i*) recover the waste heat from the chemical processes, (*ii*) cogenerate the required power for CO_2 and SNG management (i.e. electrolysis, liquefaction, storage, and injection) and (*iii*) evacuate the residual heat. It is also noteworthy that the CO_2 liquefaction unit is only strategically activated during the months in which natural gas is largely consumed, thus avoiding its activation during the periods in which its injection is preferable. In contrast, the SNG liquefaction is rather sized to operate over the entire season in which the electricity import is cheaper, thus reducing its monthly power consumption to a minimum level. Since SNG liquefaction occurs at lower temperatures, it is more energy intensive than carbon dioxide liquefaction. Thus, SNG liquefaction over short periods of time would lead to an oversizing of the liquefaction system, and thus, increased investment cost.

Tables 6 and 7 summary the results of the exergy performance indicator for both case studies 1 and 2. According to these tables, an enlarged steam network slightly hinders the overall efficiency of the integrated process studied in case study 2. Compared to the electricity import, the in-house combined power and steam generation represents an additional energy conversion step, and, thus, it is responsible for an

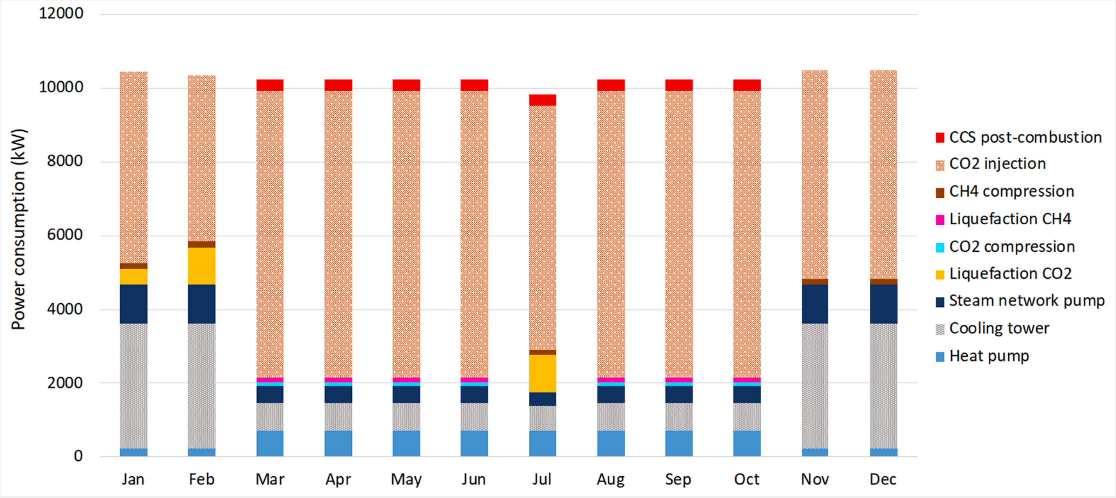

Fig. 7. Breakdown of the monthly electrical power consumption for case study 2.

Table 6
Exergy performance indicators for case study 1.

Process parameter	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Rational exergy efficiency (%)	43.55	43.55	51.83	51.83	51.83	51.83	51.83	51.83	51.83	51.83	43.55	43.55
Extended rational exergy efficiency (%)	37.57	37.57	42.66	42.66	42.66	42.66	42.66	42.66	42.66	42.66	37.57	37.57
Relative exergy efficiency (%)	36.22	36.22	49.19	49.19	49.19	49.19	49.19	49.19	49.19	49.19	36.22	36.22
Extended relative exergy efficiency (%)	31.24	31.24	40.48	40.48	40.48	40.48	40.48	40.48	40.48	40.48	31.24	31.24
Exergy destruction ($\mathrm{GJ/t_{Pulp}}$)	35.52	35.52	22.31	22.31	22.31	22.31	22.31	22.31	22.31	22.31	35.52	35.52
Extended exergy destruction ($\mathrm{GJ/t_{Pulp}}$)	45.53	45.53	32.28	32.28	32.28	32.28	32.28	32.28	32.28	32.28	45.53	45.53

Table 7
Exergy performance indicators for case study 2.

Process parameter	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Rational exergy efficiency (%)	42.60	42.49	46.69	46.69	46.69	46.69	49.29	46.69	46.69	46.69	42.67	42.67
Extended rational exergy efficiency (%)	36.25	36.25	43.89	43.89	43.89	43.89	46.57	43.89	43.89	43.89	36.25	36.25
Relative exergy efficiency (%)	35.90	35.81	36.52	36.52	36.52	36.52	39.67	36.52	36.52	36.52	35.96	35.96
Extended relative exergy efficiency (%)	31.72	31.72	35.79	35.79	35.79	35.79	39.09	35.79	35.79	35.79	31.72	31.72
Exergy destruction ($\mathrm{GJ/t_{Pulp}}$)	36.08	36.15	27.68	27.68	27.68	27.68	24.81	27.68	27.68	27.68	36.04	36.04
Extended exergy destruction ($\mathrm{GJ/t_{Pulp}}$)	46.04	46.11	40.42	40.42	40.42	40.42	35.17	40.42	40.42	40.42	46.00	46.00

increased amount of exergy destruction. Meanwhile, by importing electricity from the grid during the cheap electricity season (March-October), the extended exergy efficiencies of both case studies can be improved from 4 up to 9 percentage points. In brief, depending on the characteristics of the electricity mix, an intensive importation thereof reduces the need for internal cogeneration and, thus, it also reduces the irreversibility of both scenarios. As it concerns the exergy destruction indicator, case study 2 presents a slightly better performance, compared to case study 1, especially during the months in which electrolysis system is not activated and CO_2 storage is enabled. However, exergy destruction during the period of November-February is comparable in both case studies.

As for the environmental emissions, it is noticed that they are quite different, being case study 2 more environmentally favorable (see Table 8). In addition, the extended exergy analysis shows that, by including the upstream inefficiencies of the supply chains, the performance of the two case studies may drop 13-20% with respect to the plantwide (non-extended) performance. Thus, the inefficiencies associated with the obtainment of the energy resources should not be neglected in the early stages of the comparative analyses between the traditional and alternative setups that aim to support the decision-making.

Table 8
Indirect, direct and avoided CO_2 emissions for case studies 1 and 2.

	Case 1	Case 2
Indirect fossil CO_2 emissions (t_{CO2}/y):	82,307	93,619
• *Electricity (%)*	18.62	26.82
• *Wood (%)*	68.87	60.55
• *Chips (%)*	11.40	12.63
• *Oil (%)*	1.11	
Direct fossil CO_2 emissions (t_{CO2}/y)	24,293	–
Direct biogenic emissions (t_{CO2}/y)	281,098	236,044
CO_2 emissions avoided (t_{CO2}/y):		
• *Captured in the ammonia plant*	442,539	442,539
• *Captured in post-combustion CCS unit*	–	110,395
• *Injected*	–	535,451
Overall CO_2 balance (t_{CO2}/y)	**−54,840**	**−205,788**
Net CO_2 balance (t_{CO2}/y)	**−335,939**	**−441,832**

The yearly indirect, direct and avoided CO_2 emissions, as well as the yearly net and overall CO_2 balances for case studies 1 and 2 are also presented in Table 8. Notably, the direct CO_2 emissions from the only fossil energy resource (i.e. oil for combustion in the lime kiln) can be eliminated thanks to the use of the synthetic natural gas that is produced in the case study 2. However, the indirect emissions associated to biomass and electricity supply chains still represent a challenge for the decarbonization of the extended production process. The biomass consumption, either as fuel or feedstock, is responsible for 73% of the indirect CO_2 emissions in the case study 2, whereas the electricity import accounts for almost one-fourth of those emissions. Thus, even though both energy resources (biomass and electricity) are typically assumed as renewable in the plantwide scope, it is evident that this fact ignores that they are not emissions-free in a broader scope. This circumstance implies that not only the pulp and fertilizer sectors, but also the other economic sectors should be concomitantly defossilized to achieve a truly circular economy, based only on renewable energy resources. Others works have proposed the production of dimethyl ether, methanol, synthetic natural gas and hydrogen as renewable energy carriers for the transportation sector (Domingos, 2023; Domingos et al., 2022a, 2021a).

Table 9

Operating incomes, costs, revenues, capital costs and total cost for case studies 1 and 2.

	Case study 1	Case study 2
Operating incomes (MEur/y)		
Pulp export	228.50	228.50
Ammonia export	43.24	43.24
Electricity export	34.68	28.83
CO_2 marketed [1]	3.72	–
CO_2 injected [2]	–	53.55
Total operating incomes (MEur/y)	***310.14***	***354.12***
Operating costs (MEur/y):		
Wood import	−47.61	−47.61
Chips import	−9.70	−12.22
Oil import	−1.57	
Water import	−3.25	−3.29
Electricity import	−0.25	−0.40
CO_2 taxed [3]	−10.66	−9.36
Total operating costs (MEur/y)	***−73.04***	***−82.40***
Annualized capital cost (MEur/y)	−19.16	−36.80
Total capital and operating cost (MEur/y)	***−217.94***	***−234.92***
Total plant revenues (MEur/y)	***237.10***	***271.71***

[1] . Considering a CO_2 market price of 8.4 Eur/t_{CO2}.
[2] . CO_2 injection credit of 100 Eur/t_{CO2}.
[3] . CO_2 tax price of 100 Eur/t_{CO2}.

Considering the sustainable development scenario for ammonia production, the integration of the advanced energy systems based on renewable energy resources is expected to cut down by 75% the atmospheric emissions of ammonia production until 2050 (IEA, 2021). In this regard, the integration of the CO_2 management systems not only contributes by already reducing up to 31% the net CO_2 emissions in the case study 2, but may also help increasing the financial attractiveness of the alternative setups (see Table 9). Indeed, additional incomes from the biogenic CO_2 injection occurring in case study 2 overcome the incremental investment costs necessary to implement the proposed CO_2 management-based setup. The expectative in the long-term scenarios is that the electrolysis and the methanation technologies also become cheaper (Thema et al., 2019), which could favor further the deployment of those technologies and its integration into the existing biomass-based industrial facilities. In summary, the proposed approach capitalizes on the improvement of the electricity consumption and the storage scheduling and the rational use of the energy resources, while it encourages the recycling and the depletion of the atmospheric carbon, up to the point of offsetting the indirect emissions arisen from the hard-to-decarbonize supply chains (e.g. energy consumption during biomass transportation).

Naturally, industrial complexes are not isolated systems and depend on the environment and the market in which they are embedded. Considering that the solution requires a large availability of biomass and also a large market that can absorb the produced ammonia, the solution is better fit for economies such as those in North and South America and other Asian zones, where biomass potential is currently underexploited. Also, it is important to notice that the emissions advantages of the biomass conversion systems depend on the indirect emission arisen from the upstream supply chains associated to that feedstock. Thus, the geographical location could be limited to regions with proven experience in large biomass processing, such as Brazil, where, for instance, the largest pulp and sugar cane mills are installed.

4. Conclusions

In this work, a systematic analysis of the integration of a pulp mill and an ammonia plant with CO_2 management systems is presented. The reuse of two common byproducts, one of the pulp mill (i.e. black liquor from the wood digestion process) and other from the ammonia plant (i.e. CO_2 separated at the syngas purification unit) is studied aiming to find synergies that help increasing the energy integration and waste heat recovery of both chemical processes. In order to offset the intermittency and variable prices associated to the seasonal electricity generation during months of dark doldrums, the CO_2 streams are stored and consumed as a means to produce synthetic natural gas only when cheap electricity is available, using a power-to-gas approach that benefits from surplus electricity generation by prosumers during the remainder months. The power-to-gas system together with the liquefied gas storage units proved to be a key strategy that can supply the operation in a synergic and reliable way. The overall performance, defined by thermodynamic, economic and environmental indicators, shows to be strongly dependent on the type of energy inputs consumed (either chips or electricity), as it impacts the carbon footprint associated to the supply chains thereof. For instance, up to 80% of the indirect emissions are due to the obtainment of the biomass, which shed lights on the importance of the extended exergy and environmental analyses of the typically known as biomass-based energy conversion systems. The opportunity of injecting biogenic CO_2 emissions may actually increase the overall plant revenues by 15%, as the gain in performance with the more advanced energy management technologies allows offsetting the additional investment costs. The avoided CO_2 emissions can be also increased by 31%. Finally, the reliability of the two integrated plants is also increased, as the waste heat recovery potential is improved and the storage technologies behave as buffering systems that can compensate the seasonal intermittency of the renewable electricity generation plants.

CRediT authorship contribution statement

Meire Ellen Gorete Ribeiro Domingos: Conceptualization, Methodology, Formal analysis, Software, Writing – original draft. **Daniel Flórez-Orrego:** Conceptualization, Methodology, Formal analysis, Writing – review & editing. **Moisés Teles dos Santos:** Writing – review & editing. **Silvio de Oliveira Júnior:** Writing – review & editing. **François Maréchal:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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