Renewable Energy 219 (2023) 119396

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Process modeling and integration of hydrogen and synthetic natural gas production in a kraft pulp mill via black liquor gasification

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ARTICLE INFO

Keywords:
Black liquor
Process integration
Gasification
Hydrogen
Synthetic natural gas
Decarbonization

ABSTRACT

The black liquor gasification integrated to chemical plants has shown potential for reducing the process irreversibility and promoting the decarbonization of this industrial sector. In the integrated chemical plants proposed in this work, the purpose is co-producing pulp and gaseous fuels, either hydrogen or synthetic natural gas, in order to expand the biorefinery product portfolio and, consequently, increase the plant revenues. However, due to additional equipment and utility demands, along with the uncertainty about the prices of the commodities; the benefits of the integrated setups must be thoroughly weighed by considering thermodynamic, economic and environmental indicators before the retrofit of the existing configuration is implemented. The exergy method is used along with the energy integration technique and other financial indicators to determine whether and in which scenarios the integrated biorefineries would be more attractive. The average exergy efficiency of the integrated chemical production plants is 44%, which is higher than that of the conventional case (40%). The balance of the overall CO_2 emissions vary from 1.97 to −0.56 t_{CO2}/t_{Pulp}, for the conventional and integrated setups, respectively. An incremental financial analysis under uncertainty also shows that the hydrogen production route with partial import of electricity and carbon taxations above 60 EUR/t_{CO2} outperforms the other scenarios. Therefore, the import of electricity from low-carbon grids and the upgrade of biorefinery residues arise as key factors for ensuring the sustainable production of traditionally fossil-based chemicals under more stringent environmental regulations.

1. Introduction

In light of the environmental concerns associated to power, fuels, and chemicals production, there is a growing commitment to explore sustainable alternatives for meeting these demands. Recent approaches [1] aim to reduce the emissions and address the uncertainty of future energy prices and carbon taxes, which are likely to be implemented under stricter environmental regulations. In this context, the utilization of biomass resources through the combined introduction of biomass gasification and carbon capture technologies can be a significant driver in the decarbonization of important commodities that have historically been heavily dependent on non-renewable natural gas.

The pulp and paper industry (PPI) is an energy intensive economic activity [2]; however, unlike other sectors, the PPI has the potential to become a carbon-negative industry, since the highest share of the current CO_2 emissions have biomass origin [3]. Accordingly, there is room for improvement of its environmental performance, aside from offering an opportunity enhance its competitiveness by adding new features to its portfolio [4]. The use of low-carbon electricity, together with the reduction of the heating requirement, the diversification of the fuel and feedstock with a secure supply of biomass, the increase of the component-wise efficiency, the enhanced waste heat recovery and the black liquor gasification, are potential strategies to decarbonize or improve the energy efficiency in this sector [5,6]. In addition, the decarbonization pathways will also rely on the type and location of the mill, available resources and on-going trends [7].

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https://doi.org/10.1016/j.renene.2023.119396
Received 1 April 2023; Received in revised form 26 August 2023; Accepted 1 October 2023
Available online 10 October 2023

The most consolidated pulping process is the kraft technique, in which chemicals are used to separate the cellulose from the lignin, whereas it produces an energy byproduct called black liquor (BL). This substance may contain up to fifty percent of the energy embodied in the woody feedstock originally fed to the kraft pulp mill. A recent review presented the latest advances in promoting the black liquor valorization [8]. Akbari et al. (2018) explored nine of these pathways to convert the black liquor into value-added products by performing a techno-economic assessment (based on conversion efficiencies and electricity input reported by the literature), with sensitivity and uncertainty analyses. The better use of the black liquor can increase the economic attractiveness, and the price of the produced fuel together with the operating costs can deeply influence the internal rate of return on investment [9]. Gasification is a promising alternative to recover the black liquor energy in lieu of the conventional combustion recovery method [10]. This approach aims to produce different products from the produced syngas, such as electricity, heat and fuels, and more specifically synthetic natural gas [11] and hydrogen [12,13].

Hydrogen plays an important role as either chemical input or energy carrier. Indeed, it is largely used as feedstock in various refineries and chemicals plants and, thus, its decarbonization potential for multiple sectors (e.g. industry, transport, heating) is currently on the spotlight [14]. In practice, about 95% of the hydrogen is currently produced using coal, oil or natural gas via steam reforming [15], whereas only a small fraction is produced using alternative routes, such as water electrolysis or biomass gasification [1]. Accordingly, the production of biomass-derived synthetic natural gas has been labeled as an interesting opportunity to drop the CO_2 emissions of conventional hydrogen production and to increase the sustainability of the energy systems [16,17]. Synthetic natural gas is a versatile energy resource, since it can be used for domestic, heating and transportation applications [18]. According to the International Energy Agency [19], in the present context of market uncertainty, the natural gas prices are foreseen to remain extremely volatile, which reinforces the need of alternative pathways to overcome its limited availability, guaranteeing the supply of this important commodity.

Darmawan et al. (2018) performed a study aiming to improve the energy efficiency of hydrogen and power cogeneration using a drying evaporation system (with preheating, evaporation, and steam superheating), followed by a black liquor gasification using circulated fluidized bed, and syngas chemical looping. Compared to the conventional multiple effect evaporation and recovery boiler systems, the proposed integrated system increased the efficiency from 9-14%–69.1% (energy basis) [12]. Later, Darmawan and collaborators (2019) investigated the hydrogen and power co-production via supercritical water gasification to convert the black liquor into syngas. The syngas chemical looping has been also implemented. As a result, a relatively high energy efficiency (80%) highlighted that the black liquor gasification is a very promising energy technology [13]. However, thermodynamic performance alone did not suffice to ensure financial attractiveness of these upgraded routes.

The literature also reports the potential reduction of CO_2 emissions when using the black liquor gasification to integrate the production of hydrogen, methanol or electricity in pulp mills [20]. The results showed that hydrogen has a significantly higher potential of reduction of the CO_2 emissions, compared to methanol or electricity co-production routes [20]. Larger reductions of the CO_2 footprint could be achieved if additional carbon capture is considered. This reduction potential depends on the assumptions regarding the nature of the electricity and the transport of the energy resources [20]. Nonetheless, efforts to consolidate its attractiveness under more stringent environmental regulations and to withhold the uncertain variation of feedstock prices have not been studied.

Naqvi et al. (2010) studied the methane production via black liquor catalytic hydrothermal gasification, considering two scenarios, namely biofuel production with and without import of additional biomass to meet the power requirements. According to the authors, the alternative production route generally improves the plant performance, compared to the existing design that uses a recovery boiler [11]. Since the produced biofuel is partially consumed in the power boiler, a significant reduction in the synthetic natural gas yield (43%) was observed in the second scenario. Later, Naqvi et al. (2012) also studied the production of synthetic natural gas via oxygen-blown black liquor gasification process and direct causticization in order to replace the traditional recovery boiler. The import of additional biomass is reportedly required, so that the increase of energy consumption for additional biofuel production can be compensated [21]. Moreover, an important quantity of biogenic CO_2 can be captured. Unlike the present work, in Naqvi et al. work (2012), neither the CO_2 emissions associated with the upstream supply chains (*i.e.* the harvesting and transportation of the biomass), nor the effect of the electricity import were assessed.

To date, there is a gap in the literature for hydrogen and synthetic natural gas production via black liquor gasification, which is an underexploited feedstock that can play an important role in decarbonization scenarios. Most of the studies involving black liquor gasification are focused on component-wise analyses (e.g., recovery boiler, drying process) and neglected the plant-wide energy integration, as well as the effect of the diversification of the energy inputs, and the uncertainty about the variable feedstock costs and the economic feasibility of the assets. In addition, a detailed process integration of hydrogen and synthetic natural gas production via black liquor gasification, based on rigorous thermodynamic simulations, and environmental and economic assessments, has not been reported. In fact, the extended supply chain performance analysis is often ignored in previous works. Thus, in this work, the co-production of pulp and hydrogen or synthetic natural gas via black liquor gasification is evaluated and compared with the conventional kraft pulping processes. A holistic approach that considers extended thermodynamic and environmental performance is adopted, along with the analysis of the economic feasibility bearing in mind the uncertainties related to the market conditions. This global vision is crucial for the decision-makers to implement the most suitable energy technologies in future decarbonization scenarios.

2. Methods

Fig. 1 schematize the systematic framework used for the chemical process synthesis and optimization conducted in this work. The approach relies on the combined use of heuristics, thermodynamics and algorithmic methods to identify and assess the different configurations and the optimal solutions [60]. Different computer aided process engineering (CAPE) tools are used, including solvers for algebraic and differential equations, optimization routines, along with thermophysical properties databases and visualization tools.

The mass, energy and exergy balances for each processing route and its respective design specifications are performed in Aspen Plus® software [22]. The energy integration problem is defined and solved using the OSMOSE framework, based on the energy demands identified using the rigorous simulation models. A resourceful utility superstructure is proposed for closing the energy balance of the chemical process. The optimal solution is identified based on the minimization of the operating costs. According to Fig. 1, if no solution is retrieved, two actions can be taken. First the utilities system is revisited to verify if other technologies should be added to the superstructure or if the maximum size and the operating conditions thereof are adequate. Secondly, some modifications in the flowsheeting tool may be required in order to enhance the thermodynamic performance. With the optimal solution for the energy integration of the studied scenario identified, the setup is assessed considering the thermodynamic, economic and environmental performance indicators. This process creates a solution database that can be further compared and ranked considering different objectives, such as efficiency, CO_2 emissions, and economic performance. This step allows issuing recommendations for the decision-makers to define if the

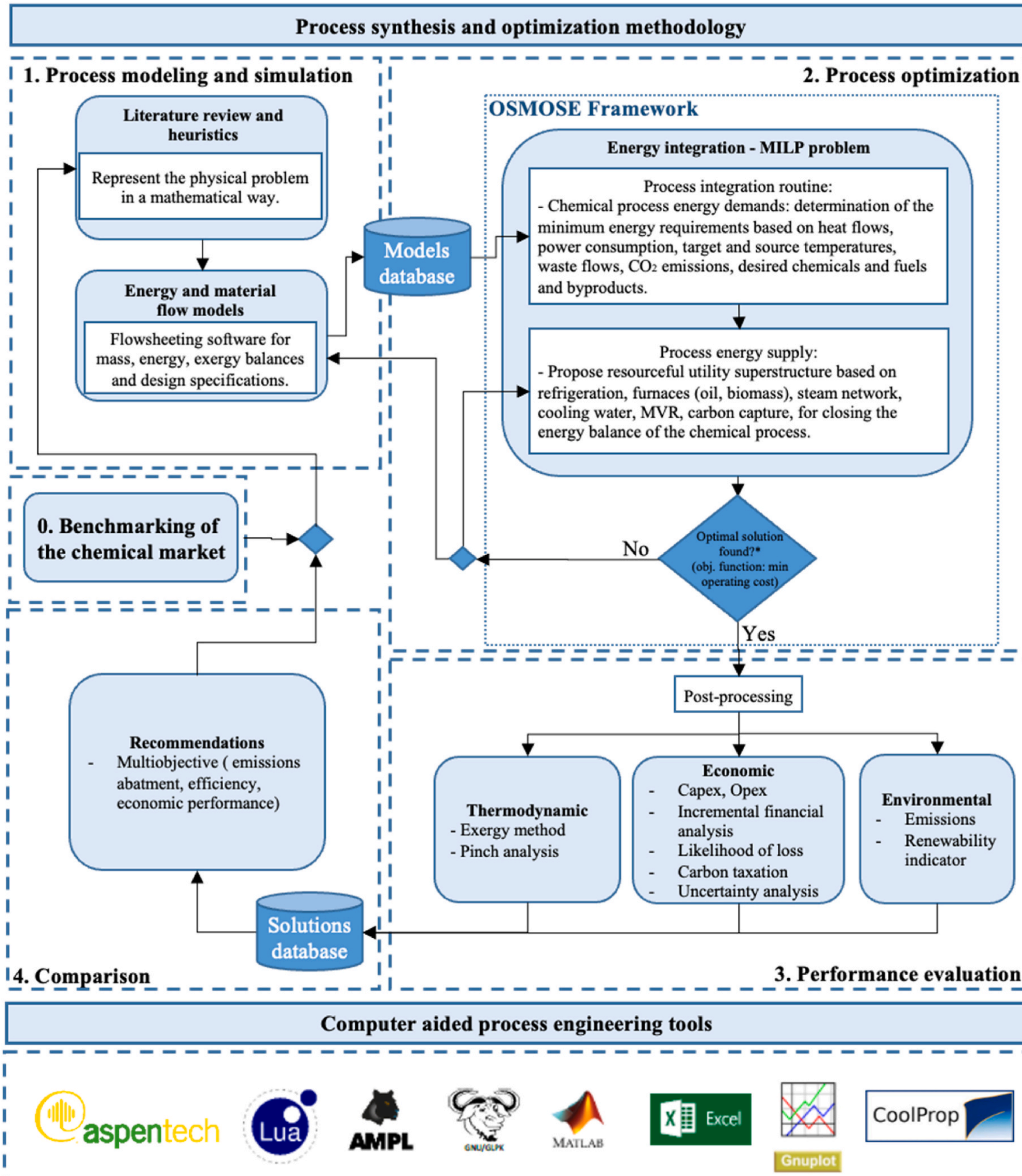

Fig. 1. Schematic of the methodology proposed and the used commercial and open source tools.

implementation of the processing route is attractive and under which conditions.

In the next sections, the methods and tools used in the process modeling, simulation and evaluation are described in more detail.

2.1. Modeling and simulation of the chemical processes and utility systems

Fig. 2 depicts the flowsheet of the kraft pulp mill integrated to the chemical production plants. The energy consumption remarks of the kraft pulp mill, as well as the details of the black liquor gasification unit and the physical-chemical data for black liquor and other substances of interest have been reported in previous works [23,24,63]. The black liquor ultimate composition (mass basis) is adopted as 29.86%C, 3.27% H, 29.05% O, 0.1% N, 4.09% S, 0.90%Cl and 32.73% Ash, whereas proximate analysis (mass basis) is considered as 85% moisture, 10.21% fixed carbon, 57.06% volatiles, and ash in balance [24].

The novelty of this work relies on the analysis of the performance of hydrogen and synthetic natural gas production, which are key feedstocks for other bulk chemical products. In this way, the analysis focuses on the impact of the specific processing steps for hydrogen and synthetic natural gas, and proposes indicators to evaluate the most profitable scenario for black liquor upgrading.

Differently from the conventional kraft pulp mill, in which multiple effect evaporators are used, in this work, an alternative drying process consisting of a mechanical vapor recompression system (MVR) is adopted. The gasifier is an entrained-flow reactor at high pressure and temperature (PEHT-BLG), operating at 30 bar and 1000 °C [61]. Then,

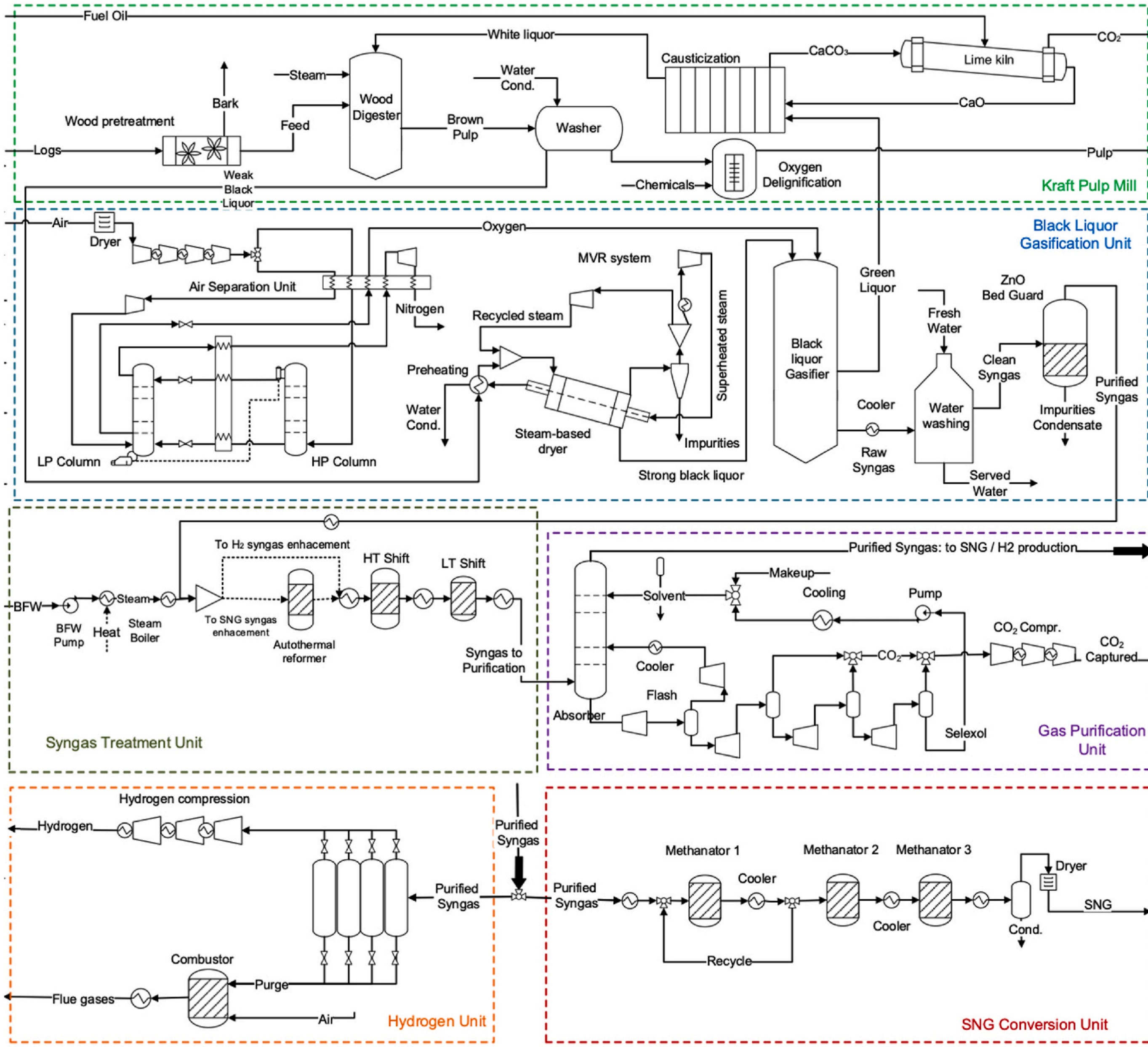

Fig. 2. Integrated flowsheet of simultaneous pulp and either hydrogen or synthetic natural gas production plants.

the syngas must go through conditioning and purification processes in order to adjust its composition and remove the undesired compounds [64]. Next, each product requires different levels of adjustment. For the hydrogen route, the syngas is fed to a water gas shift and CO_2 capture processes in order to adjust its composition aiming to maximize the hydrogen content. On the other hand, for the synthetic natural gas production, the syngas passes through an autothermal reformer, a water gas shift and a CO_2 capture system, aiming to increase CH_4 content and match the stoichiometric number [$(H_2\text{-}CO_2)/(CO+CO_2)$] approximately equal to 3 that is suitable for the later synthesis [25]. The two production options, hydrogen and synthetic natural gas routes, are described in detail in the next sections. All the conversion processes have been modeled in Aspen Plus® software. The thermodynamic model used is the Peng-Robinson equation of state with Boston-Mathias modifications (PR-BM), recommended for nonpolar or mildly polar mixtures, gas-processing and refinery [26]. To model the Selexol-based CO_2 capture unit, the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) is adopted.

2.1.1. *Hydrogen production*

The purified syngas leaving the Selexol CO_2 capture unit goes through a pressure swing adsorption (PSA) system in order to separate hydrogen from the other components. The PSA unit is simulated considering typical operating conditions (30 bar and 35 °C) [27] and assuming a hydrogen recovery efficiency of 80% mol [28]. The power consumption of the adsorption system is assumed as negligible compared to the power consumption in the downstream processes. The PSA unit is assumed as isothermal [28]. Pure hydrogen exits the PSA unit as the main product, whereas the purge gas produced can be burnt to recover its energy. Then, the purified hydrogen stream is compressed up to 200 bar for its exportation [1].

2.1.2. *Synthetic natural gas production*

The synthetic natural gas production is driven by the methanation reactions (R.1 and R.2). The methanation process consists of three sequential reactor beds wherein the catalytic conversion of hydrogen, CO and CO_2 into methane and water occurs at temperatures between

250 °C and 700 °C [20], and pressures about 30 bar. Since the methanation reaction is exothermic, an efficient heat recovery is essential for controlling the reactor temperature. To this end, bed intercooling and flow recycling are required to avoid catalyst deterioration. The gaseous mixture produced in the methanator has a high methane (>97%) and moisture content, thus, an additional dehydration process is required in order to achieve commercial standards [28].

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H = -206 \text{ kJ mol}^{-1} \tag{R.1}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H = -165 \text{ kJ mol}^{-1} \tag{R.2}$$

2.1.3. Resources

Fig. 2 also shows the energy resources (*e.g.* chips as fuel, wood as feedstock, fuel oil and electricity) that can be consumed in the integrated plants. The products and byproducts that can be manufactured and marketed (pulp, electricity, SNG and H_2) in those facilities are also presented.

The set of utility units used for the combined heat and power production in the cogeneration system are summarized next. The steam network superstructure contains a set of superheated steam headers and different draw-off levels of steam, which allows a thorough recovery and distribution of the waste heat in the chemical plant. The optimal steam levels are determined by examining the grand composite curves of the chemical processes. In this way, the thermodynamic potential associated to the waste heat exergy can be optimally exploited. In the furnace model equipped with air preheating, the combustion characteristics of the different fuels (bark, chips and oil) are considered. For the cooling tower, a specific consumption of electricity per unit of rejected heat is set as 0.021 kW_{el}/kW_{th} [29].

2.2. Performance indicators

The performance indicators used to evaluate and compare the conventional and the integrated chemical plants are defined bearing in mind different targets. The base case consists of an existing kraft pulp mill equipped with a typical recovery boiler; whereas the two alternative chemical production routes rely on the pressurized gasification technology and on the integration thereof within a conventional kraft pulp mill. Since additional energy consumption is required to guarantee the utilities supply to the integrated plants, two operational modes are analyzed. The first operation mode makes use of intensive electricity import from the grid (*i.e.* 'mixed' mode), whereas the second mode runs without electricity import (*i.e.* 'autonomous' mode).

2.2.1. Exergy performance indicators

Equations (1) and (2) define the rational and the relative exergy efficiencies, respectively. The numerator of the first definition comprises the total exergy output of the plant, including byproducts. The second definition accounts for the deviation from the theoretical performance, *i.e.* when only reversible interactions with the elements of the environment are involved in the production of pulp and chemicals. In these equations, *B* stands for exergy flow and subscript *destroyed* stands for process irreversibility, and the subscript *chemical* refers to either hydrogen or SNG. The physical and chemical exergies are calculated by using user defined scripts in Aspen Plus®.

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

$$\eta_{\text{Relative}} = \frac{B_{consumed,ideal}}{B_{consumed,actual}} = \frac{B_{chemical} + B_{pulp}}{B_{oil} + B_{wood} + B_{chips} + W_{net}} \tag{2}$$

According to Eq. (3), the renewability performance indicator [30] can be calculated as a function of the fossil exergy consumed (*fossil*), the process irreversibility, the exergy of the emissions, as well as the exergy used to deactivate and treat the wastes before released to the environment. The denominator, in turn, stands for the sum of the exergies of the renewable products, *e.g.* pulp and either hydrogen or SNG.

$$\lambda = \frac{\sum B_{product}}{B_{fossil} + B_{destroyed} + B_{deactivation} + \sum B_{emissions}} \tag{3}$$

According to Fig. 3, the renewability performance indicator classifies environmental unfavorable, reversible or highly favorable processes, depending on whether the exergy of the produced pulp and chemicals may offset the fossil, destroyed, deactivation and emissions contribution together. The indirect fossil exergy consumption of the supply chains of oil, biomass and electricity are respectively adopted as 1.0298, 0.059 and 0.3329 kJ per kJ of exergy input [31,32]. An exergy input of 1.7 kJ per kg of water to the wastewater deactivation unit is considered [33].

2.2.2. CO_2 emissions balances

Both overall and net balances of CO_2 emissions have been calculated. The first balance accounts for the total amount of CO_2 emitted, either from fossil or biogenic sources, minus the amount of CO_2 captured by the syngas purification system [62]. On the other hand, the net CO_2 balance considers that the absorption and release of CO_2 during biomass growth and conversion steps is cyclical, thus biogenic emission are regarded as neutral. The indirect CO_2 emissions associated with the fossil fuel consumption in the upstream supply chains can be assumed as 0.0029 and 0.0043 gr of CO_2 per kJ of oil and wood, respectively, and 62.09 grams of CO_2 per kWh of electricity [32].

2.3. Definition and solution to the optimization problem: a systematic framework

The revamp and integration of new technologies to an existing facility not only can improve the process performance, but also incurs a redesign of the mass and energy balances in order to deliver the new demands. In addition, since the import of a substantial amount of electricity is allowed decarbonization alternative, there will be a tradeoff between the extent of this import and the autonomous generation by the utility system. Also, the reduction of the biomass import as fuel may impact the amount of waste heat available throughout the plant and the capacity to generate power in the integrated steam networks. Accordingly, a systematic framework based on the OSMOSE Lua platform [34] is implemented to determine the minimum energy requirements and operating costs of the integrated chemical plants and their utility units. The optimization problem defined in Eq. (4) aims to identify the most appropriate utility systems and its operating conditions subject to the restrictions of mass and energy balances, Eqs. (5)–(8):

$$\min_{\substack{f_\omega, y_\omega \\ R_r, W}} \left[\begin{array}{l} f_{Chips}(B\cdot c)_{Chips} + f_{Wood}(B\cdot c)_{Wood} + f_{Oil}(B\cdot c)_{Oil} + f_{Power}(W\cdot c)_{Power} \\ -f_{Pulp}(B\cdot c)_{Pulp} - f_{chemicals/fuels}(B\cdot c)_{chemicals/fuels} - f_{CO_2}(\dot{m}\cdot c)_{CO_2} \end{array} \right] \tag{4}$$

where y_w and f_w stand for the integer and continues variables, respectively, related to the existence and size of each utility unit (ω). *W* represents the power generated or consumed by the chemical processes and the cogeneration plant, as well as the electricity imported from or exported to the grid; and *B* is the resources exergy flow rate (kW). The subscript *'chemicals/fuels'* refers to either hydrogen or SNG. *c* is the cost of the energy resources (EUR per kWh, m^3 or kg), and *R* is the heat cascaded from a higher ($r+1$) to a lower (r) temperature interval (kW), which depends on the overall heat balance, as shown next. The optimization problem defined in Eq. (4) is subject to:

The heat balance at the *r-th* temperature interval:

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

The overall power balance of the integrated plants:

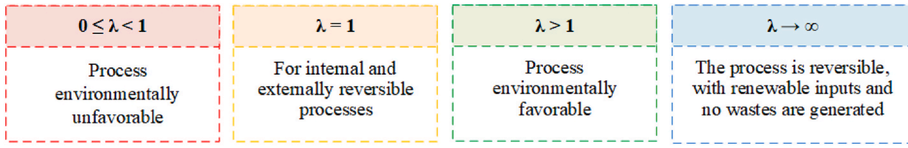

Fig. 3. Interpretation of the values of the renewability performance indicator.

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

The existence and the upper and lower bounds of the size of the utility units:

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

The feasible conditions for the energy flows in the utility system:

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

In this system of equations, N is the number of temperature intervals and N_ω is the number of units in the utility systems. Finally, Q is the heat transferred between process flows, whereas q is the heat supplied by the utility systems (kW). For economic analyses, representative costs of oil (0.018 EUR/kWh), wood (0.013 EUR/kWh), chips (0.016 EUR/kWh), electricity (0.06 EUR/kWh), hydrogen (0.072 EUR/kWh), pulp (0.144 EUR/kWh), synthetic natural gas (0.032 EUR/kWh, for non-household), and CO_2 (0.0084 EUR/kg) were considered [28,35–38].

2.4. Economic analysis

The capital expenditure (CAPEX) of the main plant equipment is estimated by correlating the capacity of each unit to a reference capacity for which the cost is known and using power scaling factors, according to in Eq. (9) [39]. The reference cost used to estimate the CAPEX of the main units are reported in Table 1. For the other equipment, such as heat exchangers, pumps, compressors and furnaces the CAPEX is estimated considering the bare module factor methodology reported in Turton et al. [39].

$$C_1 = C_0 \left(\frac{S_1}{S_0}\right)^r \tag{9}$$

For the cash flow calculations, a plant lifetime of 20 years is considered. The total CAPEX is split among the first (60%) and second (40%) years, assuming a decommissioning cost of 6% of the overall CAPEX. The operating costs (OPEX) are calculated by the methodology suggested in Turton et al. [39]. As suggested in Kangas et al. [46], the OPEX for the kraft pulp mill is considered as 4% of CAPEX. Moreover, due to the risk level associated with the technologies, it is assumed 20% as a contingency cost increment [39].

2.4.1. Incremental financial assessment

New investments are justified only if the new integrated production routes bring benefits over the conventional kraft pulp mill. Therefore, an incremental financial assessment must be addressed to elucidate the marginal gains and the conditions in which those gains are more likely to be achieved. To this end, some financial indicators are used, including the incremental net present value (INPV) assessed by Eq. (10) [47]:

$$INPV = \sum_{n=1}^{N} \frac{\left[(\text{Rev} - \text{Exp})_{n,option \ B}\right] - \left[(\text{Rev} - \text{Exp})_{n,option \ A}\right]}{(1+i)^n} \tag{10}$$

where (Rev − Exp), that is revenues minus expenses, is the net cash flow yearly evaluated at each *n-th* of the *N* periods during which the reference *(A)* and the new *(B)* setups will operate. Finally, *i* is the average interest rate (%).

The impact of the variation of the carbon taxes (0-100 EUR/t_{CO2}) and the interest rate (0–21%) on the INPV has been analyzed by means of a sensitivity analyses, aiming to explore the effect of the higher risk perception related to the new technologies, and also to take into account more stringent environmental regulations.

For the sake of comparing different economic scenarios, first, it has been considered that the costs of the feedstock and the products do not vary. This preliminary deterministic analysis allowed weighing relevant operating conditions to the plant performance without dealing yet with the uncertainty of the commodities prices. In a second analysis, the uncertainty associated to the commodities costs is incorporated to the incremental financial analysis, simulating the effect of the volatile market. To this end, the Monte Carlo method is used to simulate the stochastic variation of the prices of the commodities, assuming normal distributions with mean prices shown in Section 2.3 and standard deviation of 30%. In this way, the INPV of the integrated pulp and hydrogen (or synthetic natural gas) chemical plants can be estimated. A novel indicator considering the probability of achieving a negative INPV is calculated and defined as the 'likelihood of loss'. Table 2 summarizes the three scenarios in which the stochastic prices of commodities are considered whereas the carbon taxes are assumed from deterministic up to completely stochastic, reflecting the uncertainty of an emissions trading system. A linear increasing profile of the carbon taxes over time is also considered to emulate the gradual introduction of the taxation system. The interest rate considered in the incremental financial analysis is deterministic and can vary from 0 to 21%.

As a result, the "likelihood of loss" will be a function of the interest rates, the market prices fluctuations, and the carbon taxations. Those macroeconomic parameters can be regarded are representative of risk perception, market uncertainty and more stringent governmental regulations. bearing in mind the implications of the money depreciation in the time horizon.

Table 1
Equipment cost correlations in MUSD.

Equipment	Function	Unit of the reference variable	Source
Black liquor gasifier	$39.08\left(\frac{P}{381}\right)^{0.6}$	$MW_{Blackliquor}$	[40]
Air separation unit	$27\left(\frac{\dot{m}}{45833}\right)^{0.6}$	kg_{O2}/h	[40]
Water gas shift reactor	$1.17 * 5.77\left(\frac{V}{0.104}\right)^{0.6}$	m^3	[41, 42]
CO_2 capture unit based on Selexol®	$54.1\left(\frac{\dot{n}}{9909}\right)^{0.7}$	$kmol_{CO2}/h$	[43]
Methanator	$5.345\left(\frac{P}{175}\right)^{0.67}$, vessel $1.031\left(\frac{P}{175}\right)^{0.67}$, catalyst	MW_{SNG}	[44]
Pressure swing adsorption unit	$32.6\left(\frac{\dot{n}}{9600}\right)^{0.7}$	$kmol_{feed}/h$	[45]

3. Results and discussion

In the following sections, the performance of the integrated chemical plants producing pulp and hydrogen (H_2) or synthetic natural gas (SNG)

Table 2
Studied scenarios of stochastic commodity prices classified in terms of the variation of the carbon taxes and interest rates.

Scenario	Carbon taxes	Interest rate	Prices of commodities
i. DCTIR_SC	Deterministic (0-100 EUR/t_{CO2})	Deterministic (0–21%)	Stochastic
ii. LCT_DIR_SC	Linear increasing (0-100 EUR/t_{CO2})	Deterministic (0–21%)	Stochastic
iii. SCTC_DIR	Stochastic	Deterministic (0–21%)	Stochastic

are compared to the conventional kraft pulp mill. When the consumption of chips as fuel is as important as intensively importing electricity from the grid, the operating mode is denominated '*mixed mode*', whereas an operation in which the combined heat and power supply only depends on the chemical plant cogeneration system (*i.e.* without electricity import), the operation mode is called 'autonomous' mode.

3.1. Energy and exergy assessment

Table 3 compares the calculated processes parameters of the conventional case to those of the integrated H_2 and SNG production plants, when working under both *mixed* and *autonomous* modes. As it can be seen, the amount of chips fuel consumed to drive the utility systems of the integrated plants running under autonomous mode is sevenfold higher than the amount consumed when the mixed mode is considered. In the mixed operation mode, the electricity import from the grid is favored to supply the needs of the system. Consequently, depending on the overall efficiency of the electricity mix, the partial import of electricity may be more or less favorable than self-generating the electricity and heat in the own utility systems. The internally combined heat and power generation is justified by an enhanced utilization of the waste heat and the valorization of the biorefinery residues, so that more value-added products can be produced, whereas satisfying the utilities demands and reducing the thermal wastes.

According to Table 3, the overall exergy consumption of the integrated plants varies depending on whether the mixed or the autonomous operation mode is enabled. For instance, taking as a reference the conventional case, the scenarios of the integrated chemical plants working under the mixed mode presented an increase of 10–12% of exergy consumption, while the scenarios working under the autonomous mode exhibited up to 35% higher exergy consumption. This increment can be explained by the newly created exergy demands of H_2 and SNG production routes. Table 3 also reports the *Extended Exergy Consumption*, which can be up to 20% higher, due to the inclusion of the upstream supply change inefficiencies. This outcome is important for comparing the performance of the standalone and the integrated kraft mills with other chemical sectors. In fact, the indirect exergy consumption is typically neglected during early stages of design, but may have an important role when analyzing the life cycle performance.

As for the breakdown of the power generated and consumed in the production facilities, Fig. 4 evidences that the kraft pulp mill alone account for about half of the total power demand, regardless of the setup adopted, *i.e.* a standalone or a kraft mill integrated to a chemical plant. The mechanical vapor recompression (MVR) and the air separation unit are responsible for 23% and 13% of the overall power consumption, respectively. It can be seen that the Rankine cycle of the scenarios working under the autonomous mode must have a larger installed capacity to meet both the chemical plants demands and the ancillary power consumption (5.02–5.28 GJ/t_{Pulp}). On the other hand, for the hydrogen production route (Fig. 4b and c), the hydrogen compression for commercialization up to 200 bar represents around 4% of the power consumption. Other important remark is that the CO_2 capture system for the SNG production (see Fig. 4d and e) demands lower power compared to H_2 production. For SNG production, both CO and CO_2 are used as reactants for methanation, whereas for H_2 production the goal is to maximize the H_2 content, leading to larger production of CO_2.

Fig. 5b–e shows the *integrated composite curves* of the integrated chemical plants, which can be compared to the conventional kraft pulp mill curve (Fig. 5a). This curve exemplifies the effect of improving the black liquor evaporation system (MVR system) and the steam cycle operating pressure [48], two hypothesis already suggested by other authors [49]. The details on how these steps could be better performed for producing chemicals and fuels have nevertheless been graphically represented only in the present work. The waste heat produced along the chemical plants and that poses the largest energy recovery opportunity is represented by the self-sufficient zones known as 'pockets', in which the waste heat can be recovered either for preheating streams or raising high pressure steam. This strategy helps shortening the amount of chips

Table 3
Process parameters calculated for the conventional and the integrated kraft pulp mills, considering autonomous and mixed operation modes. Wood feedstock to digester is 41.15 GJ/t_{Pulp}, and oil consumption in the lime kiln is 1.05 GJ/t_{Pulp}.

Process parameter	Operative configuration				
Operating mode	Conventional	Mixed	Autonomous	Mixed	Autonomous
Integrated plant value-added product	None	H_2	H_2	SNG	SNG
Fuel used in the utility system	Black liquor	Electricity/Chips	Chips	Electricity/Chips	Chips
Chips consumption by utility systems (GJ/t_{Pulp})	0.00	2.13	14.95	1.19	13.24
Import of electricity as utility (GJ/t_{Pulp})	0.00	3.05	0.00	2.89	0.00
Overall plant exergy consumption (GJ/t_{Pulp})	42.20	47.37	57.14	46.28	55.44
Extended plant exergy consumption (GJ/t_{Pulp})	48.87	56.81	66.23	55.45	64.25
Power generated by the Rankine cycle (GJ/t_{Pulp})[a]	4.26	2.07	5.28	1.97	5.02
Power requirement of the kraft pulp mill (GJ/t_{Pulp})	2.84	2.84	2.84	2.84	2.84
Power requirement of the black liquor drying and gasification units (GJ/t_{Pulp})	1.20	1.20	1.20	1.20	1.20
Power requirement of the syngas conditioning and chemical plant (GJ/t_{Pulp})	0.00	0.38	0.38	0.13	0.13
Ancillary power demand (GJ/t_{Pulp})[b]	0.14	0.06	0.22	0.06	0.21
Minimum cooling requirement (GJ/t_{Pulp})	1.36	2.67	2.67	1.95	1.95
Minimum heating requirement (GJ/t_{Pulp})	8.22	2.04	2.04	1.99	1.99
Consumption of biomass ($t_{Wood}/t_{(H2\ or\ SNG)\ +\ Pulp}$)	3.23	3.22	4.17	2.97	3.82
Production of syngas (GJ/t_{Pulp})	0.00	9.36	9.36	9.36	9.36
Production of H_2 or SNG (t/day)	0.00	46.96	46.96	101.40	101.40
Production of pulp (t/day)	877.00	877.00	877.00	877.00	877.00
Production of marketable CO_2 (kg/h)	0	49,590	49,590	38,362	38,362
Electricity export (kW)	878	0.00	0.00	0.00	0.00

[a] High pressure steam 100 bar, intermediate pressure steam 12 bar, low pressure steam 4 bar and very low-pressure steam 0.10 bar, 200 °C superheating.
[b] Vapor compression refrigeration unit and cooling tower system.

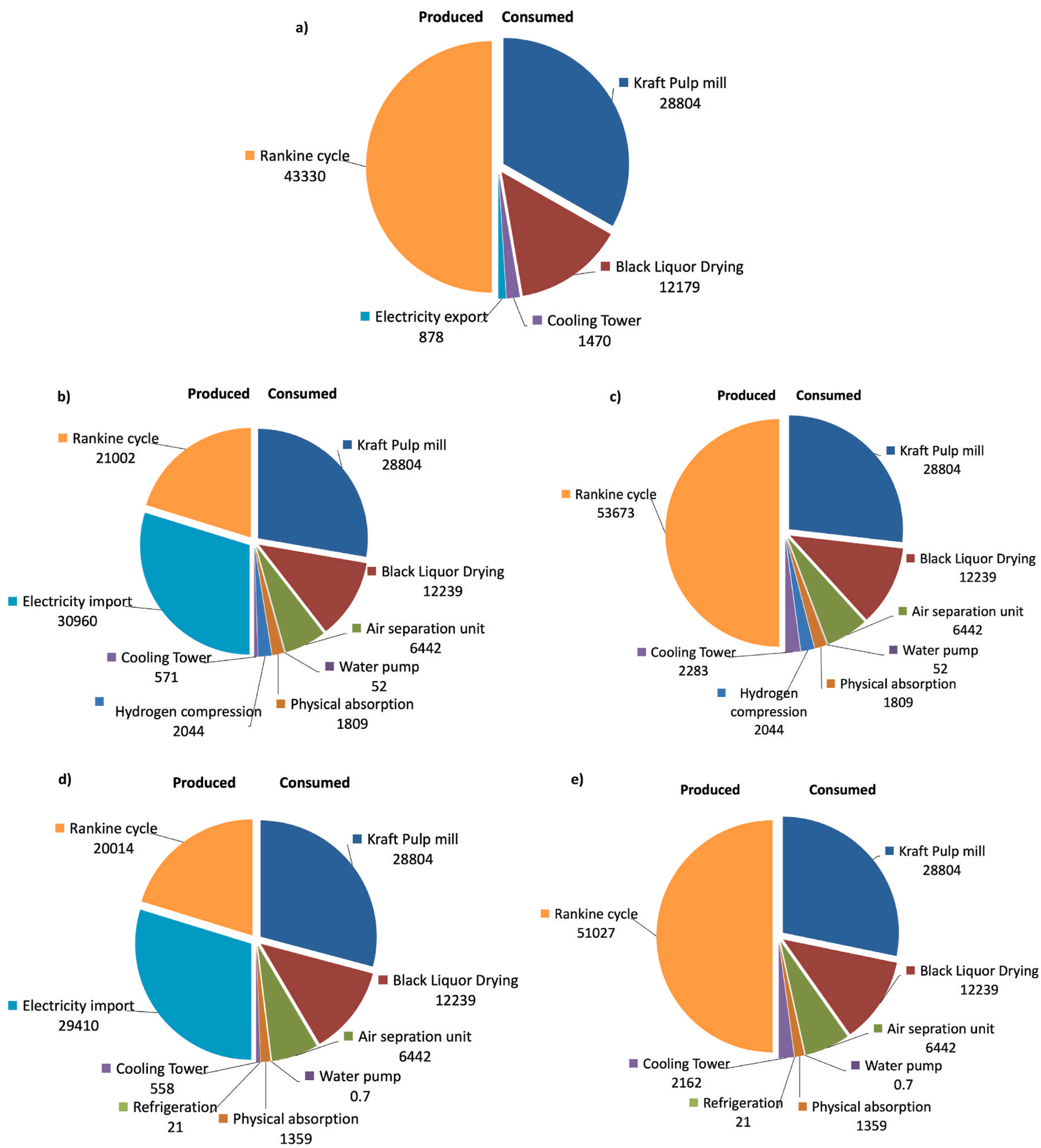

Fig. 4. Power generation and consumption (in kW): (a) conventional configuration, (b) pulp and hydrogen production running on mixed mode, (c) pulp and hydrogen production running on autonomous mode, (d) pulp and synthetic natural gas production running on mixed mode, (e) pulp and synthetic natural gas production running on autonomous mode.

used as fuel. Thus, the enhanced energy integration significantly contributes to the design of more efficient energy conversion processes in the existing facilities [17,50].

In the conventional case, the direct combustion of the black liquor and the residual bark is enough to supply the utility requirements, with a small potential to export surplus electricity, which is in agreement with other reports [48]. However, combustion entails higher exergy destruction if contrasted with the integrated chemical plants running under the mixed mode (see Table 4). This drawback is also shared with the configurations working under the autonomous mode (see Fig. 5c–e), since a supplementary amount of chips must be consumed to fully supply the energy demands of the integrated chemical plants. For the configurations running under the mixed mode (Fig. 5b–d), the quantity of chips is sharply reduced by maximizing the recovery of waste heat, whereas the largest share of the power used in the chemical plants is imported from the grid. As a consequence, the large irreversibility rates seen on the autonomous scenarios can be avoided, as the heat transfer rates are minimized (note the shorter horizontal span in the curves of Fig. 5b–d). It is clear that the advantages of the electricity import are subject to the availability of more efficient and environmentally friendly electricity mixes, which is the case of the highly renewable Brazilian electricity mix [32].

The previous results are in agreement with the exergy efficiencies summarized in Table 4. In effect, the value calculated for the conventional kraft pulp mill (39.5%) is slightly lower than the average values found for the integrated chemical plants, producing pulp and synthetic natural gas (44.2%) or pulp and hydrogen (43.6%). Other authors assessed the exergy efficiency for SNG production via wood gasification

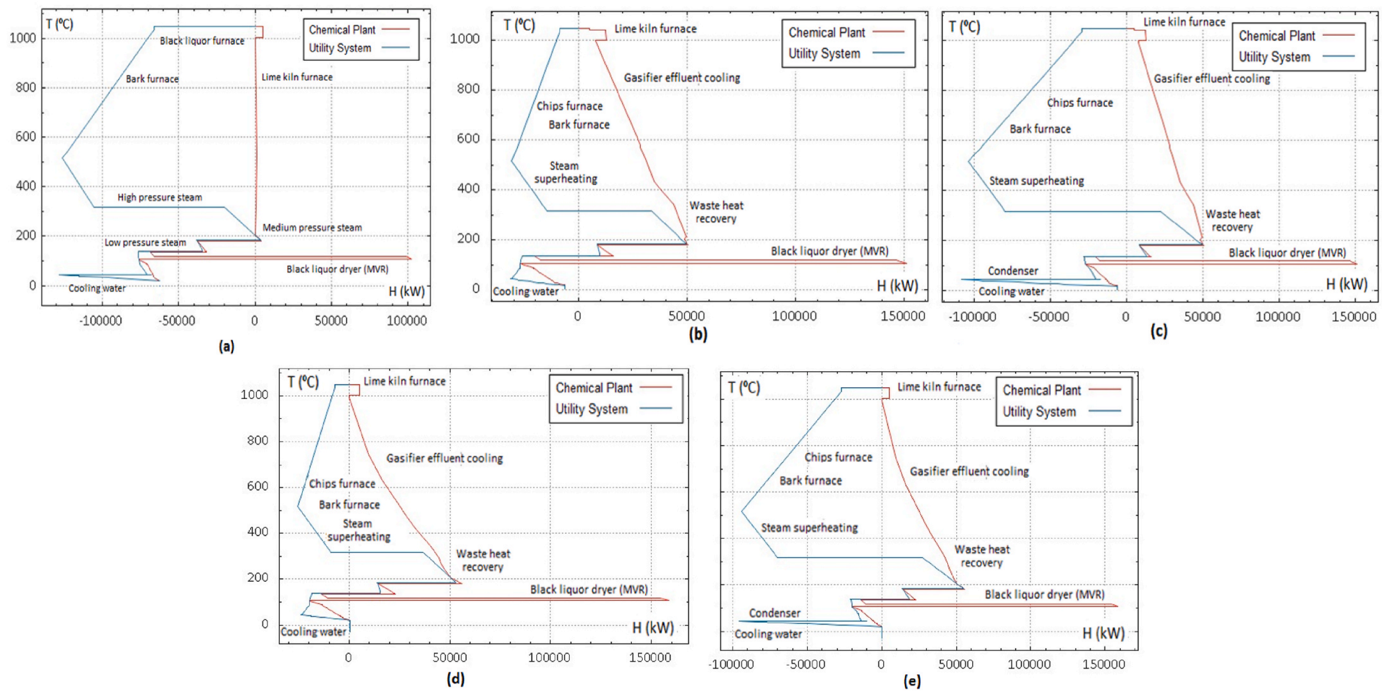

Fig. 5. Integrated composite curves: (a) conventional configuration, (b) pulp and hydrogen production running on mixed mode, (c) pulp and hydrogen production running on autonomous mode, (d) pulp and synthetic natural gas production running on mixed mode, (e) pulp and synthetic natural gas production running on autonomous mode.

Table 4
Exergy efficiencies and overall exergy destruction for the studied scenarios.

Operation mode	Conventional	Mixed	Autonomous	Mixed	Autonomous
Value-added product	–	H_2	H_2	SNG	SNG
Rational exergy efficiency (%)	42.46	52.26	43.32	52.62	43.92
Extended rational exergy efficiency (%)	36.66	43.57	37.38	43.91	37.90
Relative exergy efficiency (%)	42.25	50.97	42.25	51.59	43.07
Extended relative exergy efficiency (%)	36.48	42.49	36.45	43.06	37.16
Exergy destruction (GJ/t_{Pulp})	24.28	22.61	32.39	21.93	31.09
Extended exergy destruction (GJ/t_{Pulp})	30.96	32.06	41.47	31.10	39.90

finding values hanging between 53 and 58%, although considering the steam streams also as main products in the efficiency definition and ignoring the indirect contributions of the supply chains [51]. As it concerns the overall exergy destruction, the integrated plants running under the mixed mode also outperformed the remaining scenarios. The use of a higher renewable grid mix as well as other standalone renewable electricity sources, like solar and wind, can be an effective option to improve the exergy performance of biomass-based gasification systems [52,62]. Also, according to Table 4, when the irreversibility associated to the supply chains is considered, an important reduction of up to 19% of the exergy efficiency for all scenarios can be observed. This result confirms the fact that the extended exergy destruction due to the supply chains performance has an impairing effect on the overall performance of the integrated plants, when compared to the conventional case (30.96 GJ/t_{Pulp}). It can be explained by the lower number of energy conversion systems in the conventional case, although only at the expense of the absence of value-added products (chemicals and fuels).

3.2. Environmental analysis

The results of the overall and net balances of CO_2 emissions, including the breakdown of indirect and direct emissions, are presented in Fig. 6. Strikingly, the fossil indirect CO_2 emissions related to the supply of wood and chips represent the largest contribution to the indirect emissions (77%–99% out of 0.24 t_{CO2}/t_{Pulp}), even surpassing the contribution of the fossil direct emissions in the lime kiln. This result highlight the importance of considering the indirect emissions associated to the supply chains to achieve the decarbonization of the sector [53]. On the other hand, the increased biomass-related emissions could be cut down if more efficient biomass integrated gasification combined cycles were implemented. Yet, the use of combined cycles will also add a further degree of complexity and could render the initial investments prohibitively high.

The biogenic emissions avoided are possible thanks to the syngas purification unit integrated into the chemical production plants. This sequestration represents an opportunity to decarbonize the hydrogen and synthetic natural gas production, aside from promoting the carbon capture from atmosphere and the decarbonization of other industries that depend on those commodities [7]. In view of the negative net CO_2 emissions balance (-1.03 t_{CO2}/t_{Pulp}), it is expected a removal of one ton of CO_2 from the environment per ton of pulp produced in the integrated plants. Note also that, even if the net CO_2 emissions balance of the production routes of synthetic natural gas it is slightly higher than that

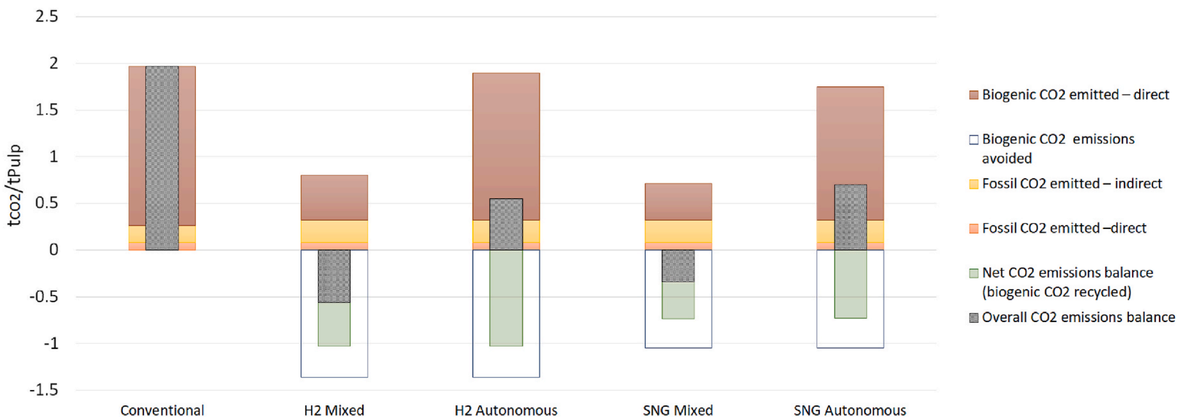

Fig. 6. Balance of CO_2 emissions for the studied scenarios.

of the hydrogen production route, this balance is also negative (−0.73 t_{CO2}/t_{Pulp}). Looking at the overall CO_2 emissions balance, the conventional case presented a positive value of 1.97 t_{CO2}/t_{Pulp} whereas the integrated cases operating under the mixed mode achieved negative values, *e.g.* −0.56 t_{CO2}/t_{Pulp} for the hydrogen route.

Based on Table 5, for the conventional kraft pulp mill, the renewability indicator (λ) can be as low as 0.64, which contrast with the λ values for the integrated chemical plants (0.91–0.92). The literature also reports λ values lower than the unity for other biorefineries, such as the ethanol production from banana and its respective lignocellulosic residues [30], and the ammonia production via gasification of the sugarcane bagasse [54]. This fact suggests that the exergy of the products would not be enough to compensate for the fossil fuel exergy, the losses and the irreversibility associated to the productive system, including the supply chains. It must be underlined that renewability indicator increases as more electricity is imported from the grid (*i.e.* mixed case). This behavior is consistent with the trend shown by the exergy efficiency and it reinforces the idea that the use of resources with a large share of renewable contribution may favor the adoption and deployment of the production of biofuels in integrated biorefineries. In this way, the renewability indicator provides valuable insights related to the sustainability of the biomass-based gasification systems not addressed by the exergy analysis alone [52].

3.3. Economic analysis considering deterministic commodities prices

A technical analysis would be incomplete if only thermodynamic and environmental performance indicators are considered. Actually, the new investment could be only justified if the proposed configurations translate into higher operating revenues coming from the drop of fuel consumption, the increase of yield of value-added products or the reduction of the atmospheric emissions.

Table 6 shows the annualized investment costs and the net plant revenues calculated by considering a fixed interest rate (6%) and a plant lifetime (20 years). As it can be seen, all the integrated chemicals production plants have higher operating revenues (1–14%), compared to the conventional scenario due to the additional value-added products. However, as it concerns the net plant revenues, *i.e.* after discounting the higher capital costs of the newly integrated chemical plants, only the integrated pulp with hydrogen production achieve positive marginal gains compared to the conventional scenario, for both operation modes (mixed or autonomous). It is worth noticing that, despite the import of costlier electricity from the grid, the hydrogen production under the mixed operation mode is seemingly favored due to a relatively higher efficiency of the Brazilian electricity mix. On the other hand, the net revenues of the integrated kraft pulp mill and SNG production plants are from 11% to 20% lower in comparison to the conventional case.

The CAPEX distribution for the integrated chemicals production plants (Fig. 7) indicates that running the integrated plants under an autonomous mode demands larger chips furnaces and bulkier Rankine cycles for producing either synthetic natural gas or hydrogen. In other words, since the electricity import is not enabled, the heat recovery steam generators and the heat exchanger network must be oversized, compared to both the conventional and the integrated plants running under the mixed mode. This fact has a direct influence in the financial feasibility of the alternative production routes. From Fig. 7, it can also be noticed the share of the syngas conditioning and purification units in the total capex breakdown for each processing route, which closely follow the behavior presented in the power consumption remarks.

Other parameters that may influence the financial feasibility are the carbon taxation and the interest rate, which effect is studied using a sensitivity analysis. First, in section 3.3.1, the prices of the commodities are assumed invariable over the project lifespan; whereas in the last section, the sensitivity analyses consider the uncertainty of the commodities prices and the carbon taxes, aiming to determine the *likelihood of the loss* for each integrated production route.

3.3.1. Sensitivity analysis of the incremental net present value subject to different carbon taxes and interest rates and considering fixed commodities prices

The net revenues of the integrated kraft pulp mills and chemical production plants depend on uncertain financial parameters which influences the behavior of the INPV. This behavior, subject to carbon taxes and interest rates varying in the range of 0–100 EUR/t_{CO2} and 0–21%, respectively, is reported in Fig. 8a–d. As expected, better INPV are attained when higher carbon taxes and lower interest rates are assumed. From Fig. 8a, a positive INPV can be achieved for the integrated kraft pulp mill and hydrogen production plant when the mixed operation mode is adopted and the carbon taxes range between 30 and 60 EUR/t_{CO2}. For the autonomous operation mode (Fig. 8b), positive INPV is only reached for carbon taxes above 85 EUR/t_{CO2} and interest rates lower than 6%. Meanwhile, for the integrated kraft pulp mill and synthetic

Table 5
Renewability indicator (λ) for the studied scenarios.

Operation mode	Conventional	Mixed	Autonomous	Mixed	Autonomous
Value-added product	None	H_2	H_2	SNG	SNG
Renewability indicator (lambda)	0.64	0.91	0.67	0.92	0.69

Table 6
Operating incomes, costs and revenues and annualized investment cost for the studied scenarios.

Operation mode	Conventional	Mixed	Autonomous	Mixed	Autonomous
Value-added product	none	H_2	H_2	SNG	SNG
Operating incomes (EUR/t_{Pulp})	714.61	850.80	850.80	775.73	775.73
Operating costs (EUR/t_{Pulp})	−153.49	−213.72	−219.92	−207.01	−212.34
Operating revenues (EUR/t_{Pulp})	561.12	637.08	630.89	568.73	563.40
Annualized investment cost (EUR/t_{Pulp})	−281.13	−321.59	−347.53	−320.77	−340.78
Net Plant Revenues (EUR/t_{Pulp})	280.00	315.49	283.36	247.96	222.61

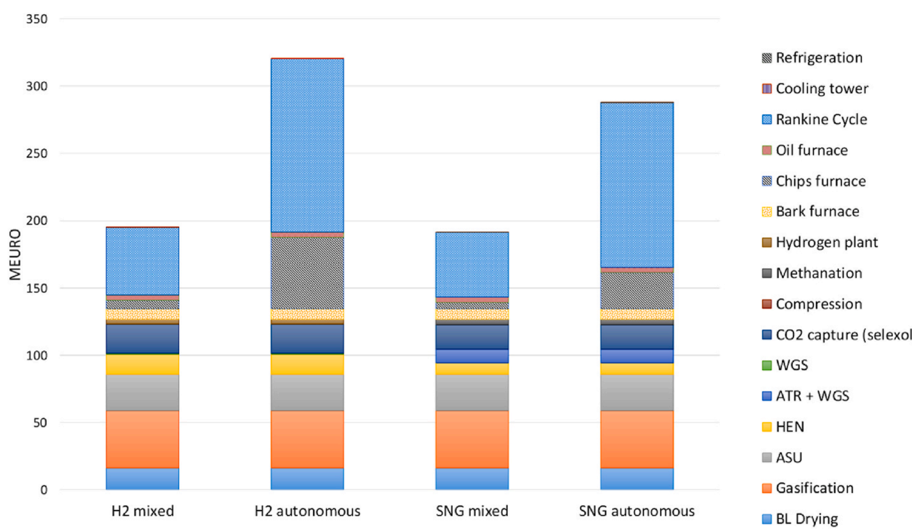

Fig. 7. CAPEX breakdown for the integrated chemicals production plants. WGS: water gas shift reactors, ATR: autothermal reformer, HEN: heat exchanger network, ASU: air separation unit.

natural gas production plants, the INPV is always negative, regardless of the operation mode (*i.e.* mixed and autonomous), as well as the carbon tax and the interest rate adopted.

3.3.2. Study of the effect of the uncertainty about the prices of the commodities on the economic feasibility using incremental financial analysis

In practice, the prices of the commodities are subject to the market volatility. In order to consider their stochastic variation, a series of Monte Carlo simulation are performed. The incremental financial analyses are based on the concept of *likelihood of loss*, defined as the probability that the incremental net present value of the integrated production routes is negative, taking as reference the net present value of a conventional kraft pulp mill.

Tables 7–10 present the heat maps with the results for the scenario *(i)* proposed in Section 2.4.1. In this scenario, it is assumed that the carbon taxes and the interest rates remain constant over time, whereas the commodities prices vary stochastically. As reported in Table 7, for the integrated kraft pulp mill and chemical plant producing pulp and hydrogen, and running under mixed mode, the probability that the INPV is positive is very high for carbon taxes higher than 60 EUR/t_{CO2}, subjected to the interest rate assumed. Yet, as the carbon tax drops and the interest rate increases, a set of Fischer interceptions becomes more evident. This region demarcates the financially unfeasible operating conditions of the integrated biorefinery concept. These tax values are in line with the current carbon taxes adopted by some countries, such as Finland or Switzerland (>70-100 EUR/t_{CO2}) [55]. In contrast, the production of hydrogen under autonomous operation mode becomes financially attractive only for the condition of the highest carbon taxes and the lowest interest rates. Meanwhile, for the integrated kraft pulp mill and synthetic natural gas production routes (Tables 9–10), the scenario is much less favorable, which can be explained by a lower market price of SNG as a value-added product in comparison to the price of hydrogen. Economic uncertainty analysis using Monte Carlo simulations for other SNG production setups considering power-to-gas approach has also been investigated by other authors [56,57]. The analysis revealed that the power-to-gas technology require significant advancement and stability in CO_2 tax credits to be economically feasible, suggesting that a life cycle assessment should be carried out to elucidate the impact of the emissions on the economic unattractiveness of the system [57]. Therefore, the Monte Carlo analysis is a relevant tool to assess the effect of the economic uncertainty in the decision-making process for the implementation of technologies with low technology readiness level and high risk perception [56].

Meanwhile, Tables 11 and 12 present the results of the *likelihood of loss* for scenarios *(ii)* and *(iii)*, respectively, defined in Section 2.4.1. The scenario *(ii)* envisages a gradual transition from zero to maximum carbon tax over the lifetime, whereas the commodities price still varies in a stochastic way. On the other hand, the scenario *(iii)* assumes that the carbon tax varies stochastically over time along with the prices of the commodities. These analyses are performed for specific (deterministic) interest rates. According to Tables 11 and 12, only the integrated kraft pulp mill and hydrogen production plant running under the mixed mode has relatively more favorable results of *likelihood of loss*. Indeed, for both scenarios *(ii)* and *(iii)*, the co-production of hydrogen will be only favored at very low interest rates (« 5%). Thus, the chemicals and fuels production through renewable biomass resources will be only boosted if other measures are complied [58,62], such as fiscal incentives and public funding towards decarbonization and cleaner energy production [59], maturation of the technologies and regulatory commitments.

4. Conclusions

In this work, thermodynamic, environmental and financial indicators are used to compare the performance of a standalone kraft pulp

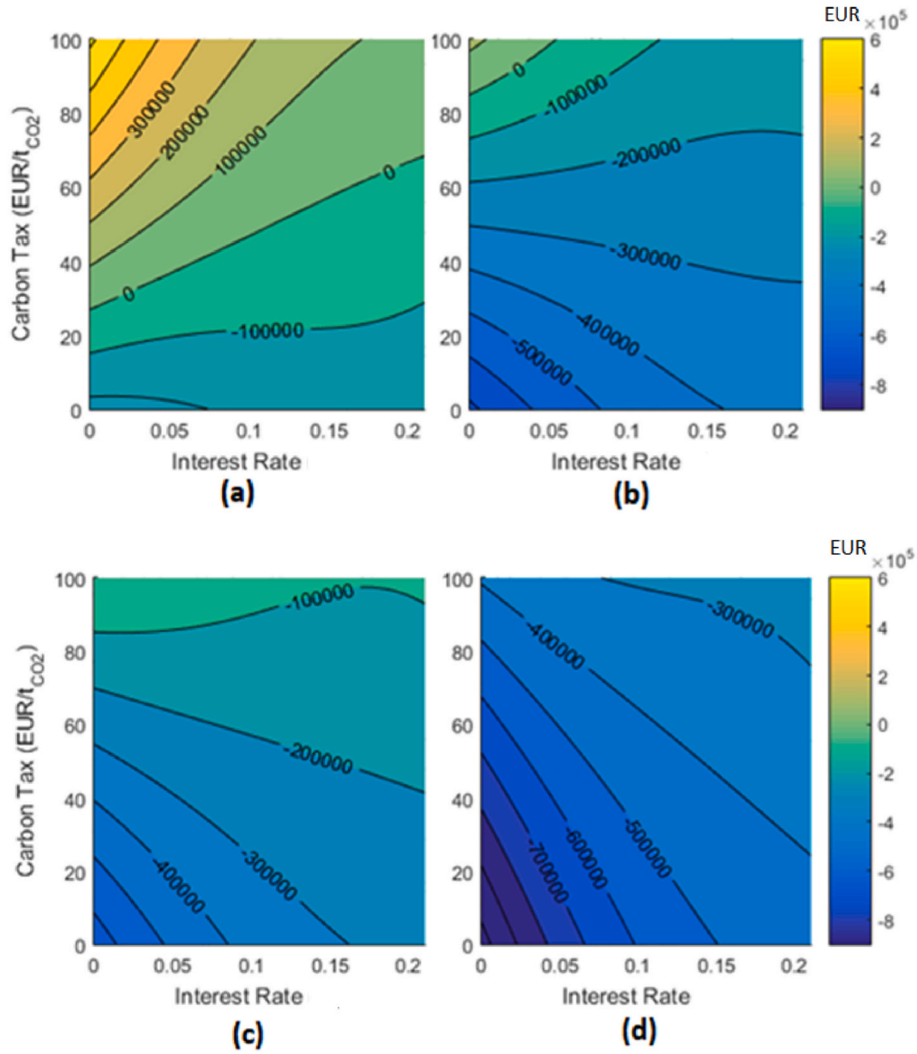

Fig. 8. INPV variation (in EUR) represented in contour plots for: (a) pulp and hydrogen production running under mixed mode, (b) pulp and hydrogen production running under autonomous mode, (c) pulp and synthetic natural gas production running under mixed mode, (d) pulp and synthetic natural gas production running under autonomous mode.

Table 7
Effect of the interest rate and the carbon tax on the *likelihood of loss* (in %) for the scenario (i) DCTIR_SC (see section 2.4.1) in which an integrated kraft pulp mill and hydrogen production plant operates under the mixed mode.

CO_2 tax (EUR/t_{CO2}) →	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**
i (%) **0%**	100	99.46	85.71	35.84	4.19	0.16	0	0	0	0	0
3%	100	99.94	96.41	63.80	14.24	0.76	0	0	0	0	0
6%	100	100	99.37	87.10	41.01	6	0.21	0	0	0	0
9%	100	100	99.94	96.86	71.41	23.47	2.09	0.04	0	0	0
12%	100	100	100	99.37	90.27	53.76	13.64	1.10	0.01	0	0
15%	100	100	100	99.84	97.14	78.64	37.23	7.30	0.46	0	0
18%	100	100	100	99.97	99.20	92.26	64.14	24.36	4.33	0.23	0
21%	100	100	100	99.97	99.89	97.37	83.20	47.30	13.97	2.16	0.14

mill to that of an integrated kraft pulp mill that co-produce hydrogen or synthetic natural gas. The integration of the chemical plants and the manufacture of the value-added products are possible thanks to the black liquor upgraded gasification system that replaces the recovery boiler. An important finding is that the possibility of importing electricity helps reducing the irreversibility, the biomass consumption, and the overall CO_2 emissions, apart from increasing the renewability performance indicator of the integrated chemical plants. In fact, the exergy efficiency of the conventional system (40%) is calculated as four percentage points lower than the average exergy efficiency of the integrated routes (44%). When the supply chain inefficiencies are considered, the extended exergy consumption could be up to 20% higher, resulting in a

Table 8
Effect of the interest rate and the carbon tax on the *likelihood* of loss (in %) for the scenario (i) DCTIR_SC (see section 2.4.1) in which an integrated kraft pulp mill and hydrogen production plant operates under the autonomous mode.

i (%) \ CO_2 tax (EUR/t_{CO2}) →	0	10	20	30	40	50	60	70	80	90	100
0%	100	100	100	100	100	100	99.96	97.40	71.34	20.30	1.29
3%	100	100	100	100	100	100	100	99.94	96.70	68.69	18.83
6%	100	100	100	100	100	100	100	100	99.81	96.79	69.91
9%	100	100	100	100	100	100	100	100	100	99.91	97.19
12%	100	100	100	100	100	100	100	100	100	100	99.93
15%	100	100	100	100	100	100	100	100	100	100	100
18%	100	100	100	100	100	100	100	100	100	100	100
21%	100	100	100	100	100	100	100	100	100	100	100

Table 9
Effect of the interest rate and the carbon tax on the *likelihood of loss* (in %) for the scenario (i) DCTIR_SC (see section 2.4.1) in which an integrated kraft pulp mill and synthetic natural gas production plant operates under the mixed mode.

i (%) \ CO_2 tax (EUR/t_{CO2}) →	0	10	20	30	40	50	60	70	80	90	100
0%	100	100	100	100	100	100	100	100	100	97.47	44.97
3%	100	100	100	100	100	100	100	100	100	99.93	88.51
6%	100	100	100	100	100	100	100	100	100	100	99.40
9%	100	100	100	100	100	100	100	100	100	100	99.97
12%	100	100	100	100	100	100	100	100	100	100	100
15%	100	100	100	100	100	100	100	100	100	100	100
18%	100	100	100	100	100	100	100	100	100	100	100
21%	100	100	100	100	100	100	100	100	100	100	100

Table 10
Effect of the interest rate and the carbon tax on the *likelihood of loss* (in %) for the scenario (i) DCTIR_SC (see section 2.4.1) in which an integrated kraft pulp mill and synthetic natural gas production plant operates under the autonomous mode.

i (%) \ CO_2 tax (EUR/t_{CO2}) →	0	10	20	30	40	50	60	70	80	90	100
0%	100	100	100	100	100	100	100	100	100	100	100
3%	100	100	100	100	100	100	100	100	100	100	100
6%	100	100	100	100	100	100	100	100	100	100	100
9%	100	100	100	100	100	100	100	100	100	100	100
12%	100	100	100	100	100	100	100	100	100	100	100
15%	100	100	100	100	100	100	100	100	100	100	100
18%	100	100	100	100	100	100	100	100	100	100	100
21%	100	100	100	100	100	100	100	100	100	100	100

reduction of the exergy efficiency for all the scenarios.

Other advantage of the integrated kraft pulp and chemical production plants is that negative overall CO_2 emissions balances (up to −0.56 t_{CO2}/t_{Pulp}) suggest a decarbonization pathway for typically fossil-based commodities through the use of biomass. The analysis included the extended and indirect exergy consumption as well as the related atmospheric emissions, which may be helpful when comparing to other chemical production routes. The techno-environomic performance exhibited a marked dependence of the indirect CO_2 emissions and the import of electricity from a cleaner grid. Indeed, the results encountered are dependent to the Brazilian electricity mix considered, and in future works would be important to expand the analysis addressing the specificities of other countries.

Moreover, due to the commercialization of the valuable hydrogen, higher operating revenues were obtained for the integrated pulp and hydrogen production plants. The uncertainty of the market prices for the commodities has been also considered, revealing that the use of constant inputs costs may lead to misleading results regarding the likelihood of loss of risky projects. For the integrated pulp and hydrogen production setup operating under the mixed mode and carbon taxes higher than 60 EUR/t_{CO2}, the probability that the INPV is positive is relatively high; or equivalently, the likelihood of loss is low (although it depends on the interest rate).

The implementation of more rigorous carbon taxes and the increase of the technological readiness levels may reduce the financial risks and give support to decision-makers in implementing biorefineries and

Table 11
Effect of the interest rate and the carbon tax on the *likelihood* of loss (in %) for the scenario (ii) LCT_DIR_SC (see section 2.4.1) in which a smooth transition from zero to maximum carbon tax is assumed over the lifespan of the integrated kraft pulp mill and H_2 or SNG production plants.

	Operation mode	mixed	autonomous	mixed	autonomous
	Value-added product	H_2	H_2	SNG	SNG
i (%)	**0%**	0.06	100	100	100
	1%	0.24	100	100	100
	2%	1.43	100	100	100
	3%	4.79	100	100	100
	4%	11.66	100	100	100
	5%	26.20	100	100	100
	6%	42.40	100	100	100
	7%	63.37	100	100	100
	8%	78.06	100	100	100
	9%	88.60	100	100	100
	10%	95.14	100	100	100
	11%	97.71	100	100	100
	12%	98.93	100	100	100
	13%	99.61	100	100	100
	14%	99.91	100	100	100
	15%	99.96	100	100	100
	16%	99.99	100	100	100
	17%	99.99	100	100	100
	18%	100	100	100	100
	19%	100	100	100	100
	20%	100	100	100	100
	21%	100	100	100	100

Table 12
Effect of the interest rate and the carbon tax on the *likelihood* of loss (in %) for the scenario (iii) SCTC_DIR (see section 2.4.1), in which a stochastic variation of the carbon tax is assumed over the lifespan of the integrated kraft pulp mill and H_2 or SNG production plants.

	Operation mode	mixed	autonomous	mixed	autonomous
	Value-added product	H_2	H_2	SNG	SNG
i (%)	**0%**	0.36	99.99	100	100
	1%	0.44	100	100	100
	2%	1.19	100	100	100
	3%	1.70	100	100	100
	4%	3.81	100	100	100
	5%	6.40	100	100	100
	6%	10.47	100	100	100
	7%	14.57	100	100	100
	8%	20.44	100	100	100
	9%	28.90	100	100	100
	10%	36.60	100	100	100
	11%	46.60	100	100	100
	12%	53.66	100	100	100
	13%	62.13	100	100	100
	14%	69.70	100	100	100
	15%	77.57	100	100	100
	16%	82	100	100	100
	17%	85.31	100	100	100
	18%	88.81	100	100	100
	19%	91.83	100	100	100
	20%	93.71	100	100	100
	21%	95.69	100	100	100

exploring new business opportunities to trigger the decarbonization of important commodities.

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 Junior:** 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.

Acknowledgements

The first would like to thank the Brazilian National Research Council for Scientific and Technological Development, CNPq (grant 142148/2019-9), the Swiss Government Excellence Scholarship (ref. 2021.0235), and the European Union's Horizon Europe Research and Innovation Programme under grant agreement No. 101084288. The second author would like to thank the Colombian Ministry of Science, Technology and Innovation – MINCIENCIAS (grant 646-2014/1128416066) and the Swiss Federal Office of Energy for funding this research work in the context of the Net Zero Lab consortium: "Sustainable natural gas (SNG) and aluminium production via biomass gasification and enhanced waste heat recovery in Novelis plant in Sierre City". The fourth author also thanks the CNPq (grant 306484/2020-0).

Nomenclature

Latin symbols

B	chemical exergy (kW)
c	costs of the exergy resources (EUR per kg, kWh or kJ)
f	unit load optimization variable (−)
H	enthalpy flow rate (kW)
HHV	higher heating value (kJ/kg)
i	interest rate (%)
LHV	lower heating value (kJ/kg)
$\dot{m}$	mass flow rate (kg/h)
$\dot{n}$	mol flow rate (kmol/h)
N	number of utility units, temperature intervals
P	power (MW)
q	thermal energy flow rate supplied by utility systems (kW)
R	thermal energy flow rate cascaded (kW)
Rev	revenues (EUR)
T	temperature (°C)
V	volume (m^3)
W	power (kW)

Greek symbols

λ	renewability exergy indicator (−)
ω	process or utility unit (-)

Abbreviations

BL	black liquor
CAPE	computer aided process engineering
DCTIR_SC	deterministic carbon taxes and interest rates, stochastic prices of the commodities
LCT_DIR_SC	linearly-increasing carbon taxes over the lifespan, deterministic interest rates and stochastic prices of commodities
MVR	mechanical vapor recompression
PPI	pulp and paper industry
PSA	pressure swing adsorption
SCTC_DIR	stochastic carbon taxes and variable prices of the commodities, deterministic interest rates
SNG	synthetic natural gas

Subscripts

BL	black liquor
exp.	exported electricity
imp.	imported electricity
r	temperature interval

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