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Decarbonizing the Fertilizers Sector: An Alternative Pathway for Urea and Nitric Acid Production

In order to alleviate the environmental impact that nitrogen fertilizers production is responsible for, several efforts have been addressed to incentivize the partial or total decarbonization of the supply chains of ammonia and its derivatives. The decarbonization of the nitrogen fertilizers sector might help not only improve its carbon footprint, but also reduce its dependence on international market prices of natural gas. To this end, in this work, two fertilizers production plants, namely nitric acid and urea, are integrated into a kraft pulp mill via black liquor gasification to supply the renewable input required by the chemical processes. The performance of the proposed systems is assessed and compared in the light of thermodynamic, economic, and environmental indicators. The choice of the utility system has been driven by the interrelation of the market conditions, as well as the extent of the energy integration of the chemical plants. As a result, the exergy efficiency of the integrated plants remains competitive against the conventional kraft pulp mill thanks to the optimal selection of the operating conditions of the utility system. This efficiency indicator compares the exergy input with the minimum theoretical work needed to reversibly produce the chemicals out from the components in the environment. Furthermore, the overall CO_2 emissions balance achieves negative values for some scenarios, pointing out the potential for atmospheric CO_2 depletion when the integrated processes are implemented. The indirect emissions of the biomass supply chain proved to have a great impact on the CO_2 balance. Finally, the findings suggest that both nitric acid and urea production have positive incremental net present values across the range of carbon taxes considered, indicating the economic viability of these integrated systems vis-à-vis the traditional standalone pulp and fertilizers production plants.
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Keywords: alternative energy sources, energy conversion systems, energy from biomass, renewable energy

Introduction

As natural gas availability decreases and its price rises, there is a growing need to explore renewable alternatives to be used as feedstock for the industrial and chemical sectors. The pulp and paper industry, as a well-established biomass-based sector, has the potential to contribute significantly in this regard. However, this industry faces industrial challenges that make it energy-intensive and responsible for approximately 2.3% of the total annual CO_2 emissions from the global industrial sector [1]. To achieve long-term sustainable growth and enhance both efficiency and profitability, integrating biorefineries into existing facilities is a promising approach [2]. Black liquor (BL), a byproduct of the kraft pulping process, holds significant potential as a feedstock for alternative assessments, as it contains over half of the energy content in the feedstock woody biomass. The syngas resulting from the BL gasification can be either harnessed for electricity generation, or it can be employed in the synthesis of chemicals and biofuels [3].

Ammonia is a highly demanded bulk chemical and, although it can be produced from syngas; currently, almost all synthetic
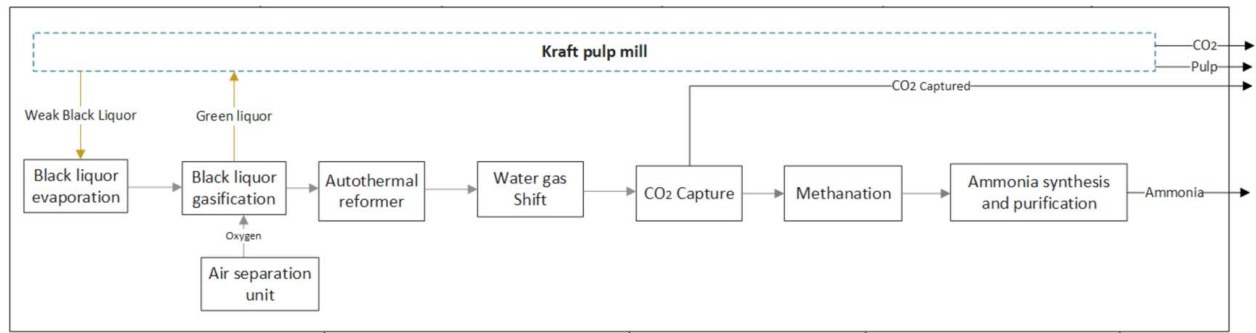
Fig. 1 Integrated flowsheet of pulp and ammonia production

fertilizers production relies on fossil fuel feedstock to obtain the required hydrogen [4]. For this reason, ammonia production is responsible for approximately 2% of the global final energy consumption and contributes to 1.3% of CO_2 emissions from the industrial systems [5]. Approximately 70% of the global ammonia production is dedicated to the manufacturing of fertilizers for the agricultural sector [5]. The production of urea, a key derivative of ammonia, accounts for over 50% of the ammonia demand. Urea is extensively used in fertilizers as a nitrogen source and serves as an important material in the food and chemical industry. Urea synthesis relies on carbon dioxide, making it an interesting route for circular carbon utilization [6]. The demand for ammonia is also driven by the production of nitric acid and ammonium nitrate. Around 75–80% of nitric acid is utilized for fertilizer manufacturing [5]. Consequently, significant efforts are underway to decarbonize the ammonia production supply chain and mitigate the environmental impacts of this sector.

Ammonia production from biomass-derived syngas is emerging more and more as a promising alternative [7]. In fact, many processing steps remain similar to those used in the natural gas-based route. In a comparative study conducted by Florez-Orrego et al. [8], conventional natural gas-based ammonia production plants were compared with a range of facilities using bagasse as a resource. The exergy efficiencies of the natural gas and biomass-based ammonia production plants were found to be 65.8% and 41.3%, respectively. Additionally, the overall emission balance varied from 0.5 t_{CO2}/t_{NH3} to −2.3 t_{CO2}/t_{NH3} for natural gas and biomass-based processes, respectively [8]. The negative values indicated the environmental benefits associated with producing chemicals using alternative energy sources like biomass. According to the authors, the opportunity of importing electricity, if available, could also help reduce the irreversibility of the systems, thus partially offsetting the inefficiencies arising from the additional biomass energy conversion processes. In the case of biomass-based ammonia production, the largest share of indirect emissions (85–100%) comes from the biomass supply, whereas the balance belongs to electricity. Consequently, the carbon footprint in the ammonia supply chain may be influenced by factors such as on-site availability and the distance required for transportation, leading to an increase in indirect emissions. Other works proposed an ammonia and nitric acid production route based on the electricity consumption in a solid oxide electrolyzer [9] and investigated optimal designs in various power supply scenarios with explicit consideration of process dynamics. According to the authors, the incorporation of nitric acid production into renewable power generation improves the operating condition of the solid oxide electrolyzer. The stack utilization increased by 30% and the specific production cost is reduced by 3%. Some works [10] have reviewed the green pathways for urea synthesis in countries with vast renewable resources. The consensus is that the skyrocketing urea prices, due to increasing shipping costs and international geopolitical tensions, may favorably boost the sustainable urea production goals. It may also initiate new business models and diversify the energy resources for those commodities. In fact,

given the current and future trends of renewable and green hydrogen cost reduction due to the incentive mechanisms and technical maturity [11], a production cost of much less than US$1000 per ton of green urea could be achieved. Notwithstanding, in view of the reduced efficiency of the biomass-based urea production route, completely green urea production is still a long way ahead from commercial application due to the higher levelized cost [12]. Accordingly, it is necessary to perform techno-economic analyses that include the uncertainty about the cost of the commodities produced and the feedstock consumed. Additionally, an extended exergy consumption analysis, including the direct and indirect, and net and overall emissions balance is necessary to help decision-makers to determine the tradeoff between biomass and natural gas-based fertilizer production routes.

Thus, this work assesses the production of nitrogen fertilizers using syngas derived from the gasification of black liquor, a byproduct of the kraft pulping process. The syngas is used to produce ammonia, which can be further used for synthesizing urea or nitric acid. The performance of these integrated plants is compared to that of conventional kraft mills in terms of thermodynamics and economic indicators, and environmental impact. An optimization framework is implemented to meet the power and heating requirements of the increased utility plant, while minimizing operating costs (OPEX). The extended exergy method, which considers inefficiencies in the upstream supply chains of different energy inputs, is also taken into account. Finally, the novelty of this study also relies on the implementation of an analysis based on the carbon taxes and market uncertainties, and discusses the implications for the decarbonization of nitrogen fertilizers.

Methods

Next, a detailed description of the modeled energy systems is presented, and the environmental and thermodynamic performance indicators are defined. The optimization methodology, used to maximize the plant revenues while maximizing the waste heat and mass recovery, is also discussed.

Process Modeling and Simulation. This section describes the modeling and simulation approach used for performing the integration of urea and nitric acid into a kraft pulp mill via upgraded black liquor gasification.

Ammonia Synthesis. Figure 1 illustrates the integrated flowsheet for pulp and ammonia production via black liquor gasification. This process is modeled in the ASPEN PLUS® software and the detailed description of this integrated system has been thoroughly discussed in Refs. [13–16].

The power and steam demands for the kraft mill are adapted from Refs. [17,18] to produce around 880 air-dried tons of pulp per day. A pulp yield of 46.51% with respect to the total amount of digested biomass is considered [19]. The respective production of black

Table 1 Ultimate and proximate analyses (wt%) of relevant streams of the gasification section and the pulp production plant

	Wood	Bark	Black liquor	Oil	Pulp
Ultimate analysis (wt%)					
Carbon	49.90	48.58	29.86	85.10	44.44
Hydrogen	6.14	5.52	3.27	10.90	6.17
Oxygen	42.85	41.19	29.05	—	49.39
Nitrogen	0.27	0.36	0.10	—	—
Sulfur	0.00	0.03	4.09	4.00	—
Chlorine	—	0.09	0.90	—	—
Proximate analysis (wt%)					
Ash	0.83	4.23	32.73	—	—
FC	—	—	10.21	—	—
Volatiles	—	—	57.06	—	—
Moisture	40	50	85	2	10
References[a]	[20,21]	[22,23]	[24]	[25]	[26]

[a]The reported values are an average of the cited literature.

Table 2 LHV and specific chemical exergy (b^{CH}) of relevant streams of the gasification section and the pulp production plant

Material	LHV (MJ/kg dry)	b^{CH} (MJ/kg dry)
Wood	18.85	21.23
Bark	17.90	20.13
Black liquor	10.28	12.08
Oil	40.56	43.38
Pulp	16.32	19.80

liquor is 1.44 t_{BL}/t_{pulp}. The ultimate and proximate analyses for the substance composition, as well as the lower heating values (LHV) of the main inputs and outputs of this process, are reported in Tables 1 and 2, respectively.

First, the weak black liquor coming from the kraft process is dried. In the conventional process, multiple effect evaporators (MEEs) are used, usually with four to six effects [17]. This system has a larger steam consumption, offering the possibility of reducing the costs by lowering the energy requirements [27]. In this regard, Darmawan et al. [28] proposed a mechanical vapor recompression (MVR) system that replaces steam input for BL concentration by an electricity input. In the present study, the conventional multiple-effect evaporator system is also replaced by an MVR system.

Next, the strong black liquor is gasified in an entrained flow pressurized reactor using oxygen (30 bar, 1000 °C). The system produces syngas, but it needs to be treated, purified, and its composition adjusted to meet the required specifications (H_2/N_2 ratio of 3:1) before en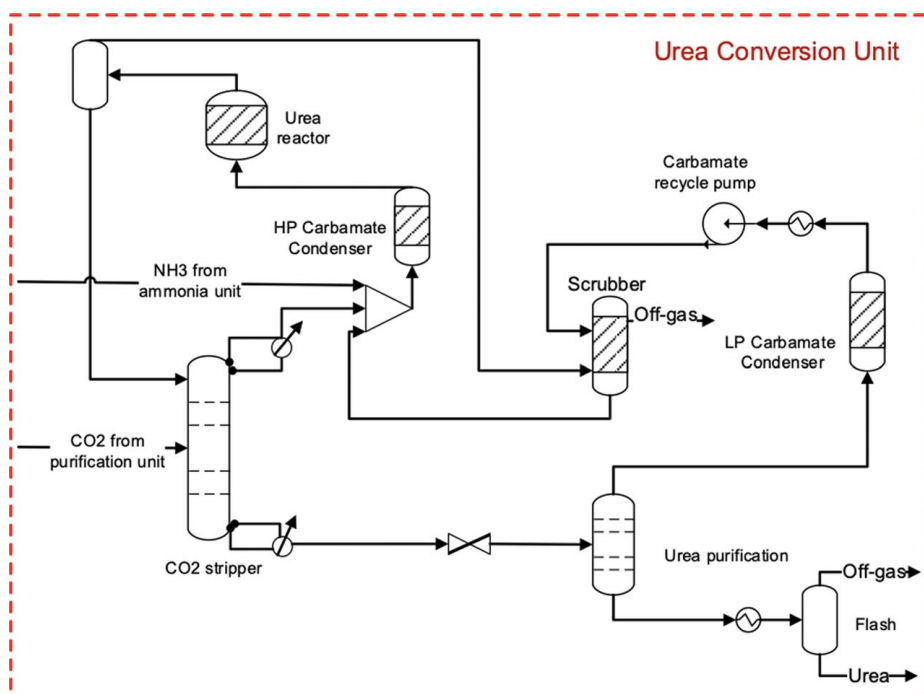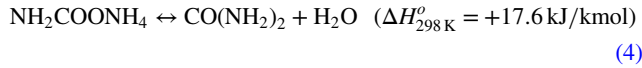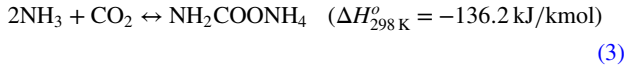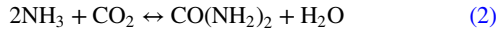tering the ammonia synthesis process. To this end, an auto-thermal reformer, a series of water gas shift reactors, a CO_2 capture unit, and a methanation system are required. The purified syngas is compressed up to 200 bar and fed to a series of sequential catalytic beds indirectly cooled, where an H_2/N_2 mixture is partially converted into ammonia [29]. The ammonia synthesis reaction is represented in Eq. (1). Finally, ammonia is purified before it follows to its end-use. The ammonia produced will be used as a feedstock either to synthesize urea or nitric acid, which specific synthesis processes will be described in the next sections.

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad (\Delta H^o_{298\,K} = 92\,kJ/kmol) \tag{1}$$
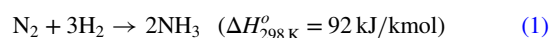
Urea Synthesis. Urea synthesis is commercially based on the Basarov reaction (Eq. (2)), which occurs between 125–250 bar and 170–220 °C in the form of two sequential reactions, namely the formation of ammonium carbamate (NH_2COONH_4) (Eq. (3)) and the dehydration of ammonium carbamate, in order to generate urea ($CO(NH_2)_2$) (Eq. (4)). The ammonium carbamate formation is highly exothermic and fast, and the chemical equilibrium is reached under the operating conditions in the reactor. On the other hand, the dehydration of ammonium carbamate is endothermic and its rate is slow and equilibrium is usually not reached in the reactor. The SR-POLAR thermodynamic model is used for simulating the urea conversion unit (Fig. 2), which is suitable for high-pressure (HP), high-temperature operating conditions. The details of the simulation approach for the urea model are described in Ref. [30].

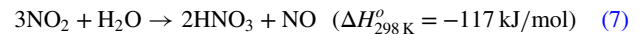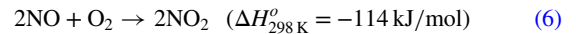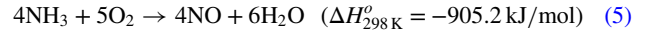**Fig. 2 Flowsheet of the urea production section**

$$2NH_3 + CO_2 \leftrightarrow CO(NH_2)_2 + H_2O \tag{2}$$

$$2NH_3 + CO_2 \leftrightarrow NH_2COONH_4 \quad (\Delta H^o_{298\,K} = -136.2\,kJ/kmol) \tag{3}$$

$$NH_2COONH_4 \leftrightarrow CO(NH_2)_2 + H_2O \quad (\Delta H^o_{298\,K} = +17.6\,kJ/kmol) \tag{4}$$

The CO_2 coming from the ammonia purification unit shown in Fig. 1 is compressed to 141 bar and fed to a CO_2 stripper to contact the urea solution coming from the reactor. In the stripper, ammonium carbamate decomposes, releasing more NH_3 and CO_2 to be stripped out. The outlet liquid solution from the stripper is rich in urea and goes to the low-pressure (LP) urea purification section, obtaining an aqueous urea solution of 77 wt%. The mixture from the top of the urea purification unit is sent to the LP carbamate condenser to compound ammonium carbamate, which is further cooled before it passes through an HP ammonium carbamate circulating pump. The mixture follows to a scrubber where the off-gas is separated and eventually, the reactants go back to the urea reactor to complete the loop.

In the adiabatic urea reactor, an aqueous solution of NH_3 and CO_2, mostly in the form of ammonium carbamate, together with light components, flows upward through the reactor volume to minimize back-mixing and provide sufficient residence time for urea formation. In the reactor, the condensation of the remaining gases occurs along with the decomposition of the carbamate to provide heat for the slightly endothermic conversion reaction of carbamate into urea. The urea solution goes back to the CO_2 stripper, while the unreacted gases follow to the scrubber. In the latter, the recycled carbamate solution absorbs the unreacted NH_3 and CO_2, while inert gases are purged in the off-gas stream. The solution at the bottom of the scrubber is next mixed with the top vapor stream from the CO_2 stripper together with the ammonia feed stream.

Nitric Acid Synthesis. Figure 3 illustrates the flowsheet of the nitric acid production. This process occurs via the Ostwald process. First, ammonia is oxidized to nitric oxide in the converter (Eq. (5)), in the presence of platinum or rhodium catalyst at high temperatures (800–900 °C) and pressure (9 bar) [31]. Nitric oxide is next reacted with the oxygen in air to form nitrogen dioxide (Eq. (6)). This step requires gas intercooling to shift equilibrium toward NO_2 formation, whereas giving the sufficient residence time to allow the homogeneous oxidation reaction to complete [31]. An increase of NO oxidation rate at temperatures around 300 °C results in an additional recovery of the heat of reaction at temperatures in which high-pressure steam can be produced. Next, NO_2 is subsequently absorbed in water to form nitric acid and nitric oxide in the absorption tower (Eq. (7)). In this way, the obtained solution of nitric acid is commercial grade (65 wt%). The tail gas from the absorption column is treated in a tail gas reactor before it is discharged [31]. The thermodynamic models NRTL-RK, ELECNRTL, and STEAMNBS are considered to calculate the thermodynamic properties of the substances and to estimate the energy conversion demands in each component.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (\Delta H^o_{298\,K} = -905.2\,kJ/mol) \tag{5}$$

$$2NO + O_2 \rightarrow 2NO_2 \quad (\Delta H^o_{298\,K} = -114\,kJ/mol) \tag{6}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad (\Delta H^o_{298\,K} = -117\,kJ/mol) \tag{7}$$

Optimization Problem Definition. The integration of the urea and nitric acid plants to the kraft pulp mill could lead to completely different utility demands. Thus, the alternatives available for supplying these demands must be evaluated [32,33], including the effect of importing either more electricity or biomass to balance the process' needs. The OSMOSE Lua platform [34] is used to calculate the minimum energy requirements (MER) of the chemical plants. It handles the mixed integer linear programming (MILP) problem that works out the best energy technologies and the operating conditions that decrease the operating costs. ASPEN PLUS® software is used to simulate the chemical plants and transfers data to OSMOSE Lua to build the MILP problem described in Eqs. (8)–(12). AMPL suite is used to solve the optimization problem [34]. The integer variables, y_w, related to the existence of a utility unit, ω, and its respective continuous load factor, f_w, can be determined by the minimization of the objective function given by Eq. (8):

$$\min_{\substack{f_\omega,\ y_\omega \\ R_r,\ W}} \begin{bmatrix} f_{Chips}(B \cdot c)_{Chips} + f_{Wood}(B \cdot c)_{Wood} + f_{Oil}(B \cdot c)_{Oil} + f_{Power}(W \cdot c)_{Power} \\ -f_{Pulp}(B \cdot c)_{Pulp} - f_{Chemical}(B \cdot c)_{Chemical} - f_{CO_2}(\dot{m} \cdot c)_{CO_2} \end{bmatrix} \tag{8}$$

Subject to
Heat balance at the temperature interval r

$$\sum_{\omega=1}^{N_\omega} f_\omega q_{\omega,r} + \sum_{i=1}^{N} Q_{i,r} + R_{r+1} - R_r = 0 \quad \forall r = 1..N \tag{9}$$

Produced and consumed power balance

$$\sum_{\omega=1}^{N_\omega} f_\omega W_\omega + \sum_{chemical\ units} W_{net} + W_{imp} - W_{exp} = 0 \tag{10}$$

Utility unit existence and load

$$f_{\min,\omega} y_\omega \leq f_\omega \leq f_{\max,\omega} y_\omega \quad \forall \omega = 1..N_\omega \tag{11}$$

Solution feasibility (MER)

$$R_1 = 0,\ R_{N+1} = 0,\ R_r \geq 0 \text{ and } W_{imp} \geq 0,\ W_{exp} \geq 0 \tag{12}$$

where

N is the number of intervals of temperature depending on the supply and target temperatures of the various streams;

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

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

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

B is the exergy flowrate of the mass and energy streams (kW);

q is the cooling or heating flowrate supplied by the utility systems (kW);

W is the power produced by the utility systems, chemical processes, or exported to/imported from the grid (kW).

The prices of feedstock, consumed/produced electricity, or marketable products (i.e., pulp, nitric acid, or urea) and byproducts (e.g., CO_2) are defined in Table 3 (EUR per kiloWatt hour or per kilogram).
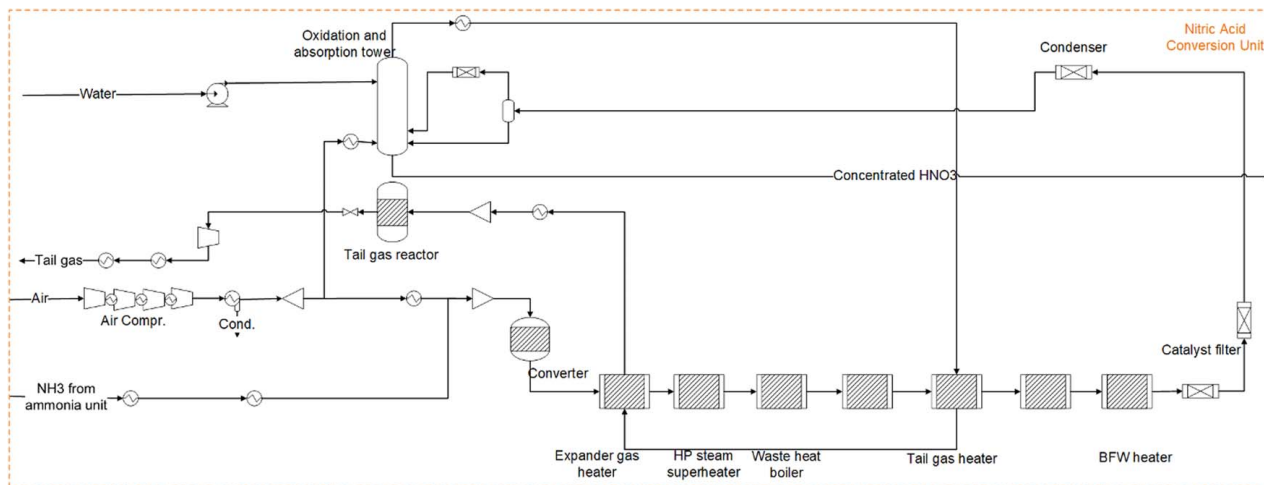
Fig. 3 Flowsheet of the nitric acid production section

Table 3 Market costs and selling prices for feedstock and products of the integrated kraft pulp mill, nitric acid, and urea production plants

Feedstock/Products	Market cost/selling price	Reference
Wood	0.013 EUR/kWh	[35]
Chips	0.016 EUR/kWh	[35]
Oil	0.018 EUR/kWh	[17]
Electricity	0.045 EUR/kWh	[17]
Pulp	0.144 EUR/kWh	[36]
Nitric acid	1.68 EUR/kWh	[37]
Urea	0.291 EUR/kWh	[38]
CO_2	0.0084 EUR/kg	[39]

Performance Indicators. In this section, the performance indicators proposed to compare the conventional kraft pulp mill (multiple effect evaporation and recovery boiler) with the BL integrated gasification systems (i.e., pulp and urea or pulp and nitric acid production plants) are defined.

Exergy Efficiency. The relative exergy efficiency indicator is defined in Eq. (13), and it quantifies the deviation from the minimum theoretical exergy consumption necessary to make up the main industrial products, i.e., pulp and chemical fertilizers.

$$\eta_{\text{Relative}} = \frac{B_{consumed,ideal}}{B_{consumed,actual}} = \frac{B_{chemical} + B_{pulp}}{B_{oil} + B_{wood} + B_{chips} + W_{net}} \quad (13)$$

where B (kW) is the exergy flowrate, and the subscripts indicate the different inputs and the main outputs of the plant. The calculation of

the physical and chemical exergy is performed using Excel spreadsheets embedded in ASPEN PLUS®.

CO_2 Emissions Assessment. Both overall and net CO_2 emissions balances are performed. The overall CO_2 emissions balance (Eq. (14)) is determined by assuming that the released CO_2, whether from fossil or biogenic sources, is offset by the avoided CO_2 captured through the syngas purification unit. In other words, in the overall CO_2 emissions balance, the biogenic emissions are also accounted as emissions from the plant. This approach allows the assessment of a more conservative scenario, enabling the identification and recommendation of measures to mitigate these emissions. On the other hand, the net CO_2 emissions balance (Eq. (15)) assumes that the CO_2 embodied in the crops ($Biogenic_{emissions}^{direct}$) entails circular emissions; thus, it is subtracted from the overall emissions. The indirect non-renewable CO_2 emissions take into account those generated at the upstream supply chains of the electricity (62.09 g_{CO2}/kWh), wood (0.0043 g_{CO2}/kJ$_{Wood}$), and oil (0.0029 g_{CO2}/kJ$_{Oil}$), according to the Brazilian electricity mix profile reported in Refs. [40,41]. The biogenic emissions consist of those originating from the combustion of woody biomass (bark and chips), depending on the respective carbon content.

$$\begin{aligned} \text{Overall } CO_2 emissions = {} & Fossil_{emissions}^{direct} + EE_{emissions}^{indirect} \\ & + Wood_{emissions}^{indirect} + Oil_{emissions}^{indirect} \\ & + Biogenic_{emissions}^{direct} - CO_2 captured \end{aligned}$$

$$(14)$$

Table 4 Correlations of the investment cost for the process units

Unit	C_{inv}	Flow	Source
Ammonia plant with BL gasification	$179.9\left(\frac{\dot{m}}{9122}\right)^{0.65}$ (MEUR)	$\dot{m}_{NH3}$ (kg$_{NH3}$/h)	[44]
Urea plant	$12.96\left(\frac{\dot{m}}{477.34}\right)^{0.65}$ (MEUR)	$\dot{m}_{Urea}$ (t$_{urea}$/d)	[12]
Nitric acid plant	$8\left(\frac{\dot{m}}{274}\right)^{0.6}$ (MEUR)	$\dot{m}_{NH3}$(t$_{HNO3}$/d)	[45]
Furnaces	200 (EUR/kW)	$\dot{m}_{fuel\_load}$(kW)	[46]
Refrigeration	750 (EUR/kW$_{th}$)	$\dot{m}_{fuel\_load}$(kW)	[39]
Cooling tower	$746.749F_{in}^{0.79}R^{0.57}A^{-0.9924}(0.022T_{wb} + 0.39)^{2.447}$ EUR[a]	—	[47]

[a]Cooling water cost estimation: F_{in} is the water flowrate in t/h, R is the range in K, A is the approach in K, and T_{wb} is the wet bulb temperature in °C.

Table 5   Scenarios and assumptions adopted for the variations in carbon taxes, interest rates, and commodity prices in the incremental financial analysis

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

$$\text{Net } CO_2\,emissions = Fossil_{emissions}^{direct} + EE_{emissions}^{indirect}$$
$$+ Wood_{emissions}^{indirect} + Oil_{emissions}^{indirect} - CO_2 captured \tag{15}$$

Equations (16) and (17) illustrate how the indirect and direct emissions are calculated, respectively.

$$m_{emissions}^{indirect}(kg_{CO2}/s) = m_{Fuel}(kg_{Fuel}/s)*b_{Fuel}(kJ_{Fuel}/kg_{Fuel})$$
$$* \frac{r_{Fuel}}{1000}(g_{CO2}/kJ_{Fuel}) \tag{16}$$

$$m_{emissions}^{direct}(kg_{CO2}/s) = m_{Fuel}(kg_{Fuel}/s)*C_{Fuel}(kg_C/kg_{Fuel})$$
$$* \frac{M_{CO2}}{M_C}(kg_{CO2}/kg_C) \tag{17}$$

where r (g_{CO2}/kJ_{fuel}) is the indirect CO_2 emissions factor, M is the molecular mass (kg/kmol), and C_{Fuel} (%) is the percentage of carbon for each fuel reported in Table 1. The biomass and fuel consumption are calculated considering the LHV and b^{ch} presented in Table 2. φ is defined as the ratio of the chemical exergy to the lower heating value ($\varphi = b^{ch}$/LHV) [42].

Economic Analysis. The investment cost of the main plant equipment is estimated by comparing the capacity of each unit to a known reference capacity and applying power scaling factors (Eq. (18)) [43]. Table 4 provides the references used for estimating the capital expenditure (CAPEX) of the main units.

$$C_{inv} = C_0 \left(\frac{S_1}{S_0}\right)^r \tag{18}$$

where S_0 denotes the reference capacity with a known capital cost C_0, while S_1 represents the actual capacity for which the capital cost C_{inv} is calculated. Additionally, the power scaling factor, denoted as r, can range between 0.5 and 0.9 depending on the specific process, as shown in Table 4.

The cash flow calculations are based on a plant lifetime of 20 years. The total CAPEX is divided between the first year (60%) and the second year (40%), with an overhead of 6% allocated to decommissioning costs. The OPEX are determined using the methodology recommended in Ref. [43]. For the kraft pulp mill, the OPEX is assumed to be 4% of the CAPEX, as suggested in Ref. [48]. To account for the associated risk level of the technologies involved, a contingency cost increment of 20% is assumed [43].

Incremental Financial Analysis Under Uncertainty of the Commodities Prices. When considering investments in new technologies, their attractiveness is determined by the advantages they offer compared to conventional setups. In order to assess the

Table 6   Energy consumption remarks and optimal process variables of the different production facilities

Process parameter	Conventional MEE	Nitric acid—mixed	Nitric acid—autonomous	Urea—mixed	Urea—autonomous
Energy resources	Chips	Electricity/Chips	Chips	Electricity/Chips	Chips
Feedstock wood consumption (GJ/t_{Pulp})	41.15	41.15	41.15	41.15	41.15
Utility chips consumption (GJ/t_{Pulp})	0.00	0.00	6.23	0.00	11.96
Utility electricity consumption (GJ/t_{Pulp})	0.00	2.13	0.00	4.08	0.00
Oil consumption (GJ/t_{Pulp})	1.05	1.05	1.05	1.05	1.05
Overall plant consumption (GJ/t_{Pulp})	***42.20***	***44.32***	***48.43***	***46.28***	***54.15***
Extended plant consumption (GJ/t_{Pulp})[a]	***48.87***	***52.70***	***56.11***	***56.21***	***62.76***
Rankine cycle power generation (GJ/t_{Pulp})[b]	4.32	3.64	5.85	2.02	6.26
Chemical process power demand (GJ/t_{Pulp})					
KraftPulp mill	2.84	2.84	2.84	2.84	2.84
Black liquor treatment and gasification	0.00	1.20	1.20	1.20	1.20
Syngas Conditioning and Ammonia Synthesis	0.00	0.77	0.77	1.19	1.19
Ancillary power demand (GJ/t_{Pulp})[c]	0.07	0.32	0.41	0.24	0.39
Cooling requirement (GJ/t_{Pulp})[d]	2.81	7.60	7.60	2.74	2.74
Heating requirement (GJ/t_{Pulp})[d]	12.80	0.00	0.00	0.45	0.45
Biomass consumption ($t_{Wood}/t_{Chemical + Pulp}$)	3.23	1.67	1.93	2.37	3.06
Syngas production (GJ/t_{Pulp})	0.00	9.36	9.36	9.36	9.36
Chemical production (t/day)	0.00	812.77	812.77	316.34	316.34
Pulp production (t/day)	877.83	877.83	877.83	877.83	877.83
Marketable CO_2 production (kg/h)	0	50,518	50,518	37,883	37,883
Electricity export (kW)	14,369	0	0	0	0

Note: Bold values show the overall and extended plant consumption. They are the sum of the energy flows of the plant-wide and extended control volumes.
[a]The overall exergy consumption increases if the extended exergy efficiency of the electricity generation (55.68%), as well as of the oil (95.20%) and biomass (86.13%) supply chains are considered [30,31].
[b]Steam pressure levels 100, 11.5, 3.8, 1.5, and 0.10 bar, steam superheating 200 °C.
[c]Cooling tower and vapor compression refrigeration systems.
[d]Heating requirements of the chemical processes (energy basis) determined from the composite curves.

incremental financial impact and identify the conditions under which these gains are most likely to be achieved, an incremental financial analysis is conducted. This analysis utilizes various financial indicators, such as the incremental net present value (INPV), which is calculated using Eq. (19):

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

(19)

where the net cash flow denoted as (Rev − Exp) represents the difference between revenues and expenses, calculated for each year n of the N yearly periods during which the reference (A) and the new (B) setups operate. Additionally, i represents the average interest rate.

A sensitivity analysis was conducted to examine the impact of carbon taxes (0–100 EUR/t$_{CO2}$) and interest rates (0–21%) on the INPV. This analysis aims to explore the higher risk perception associated with new technologies and accounts for stricter environmental regulations.
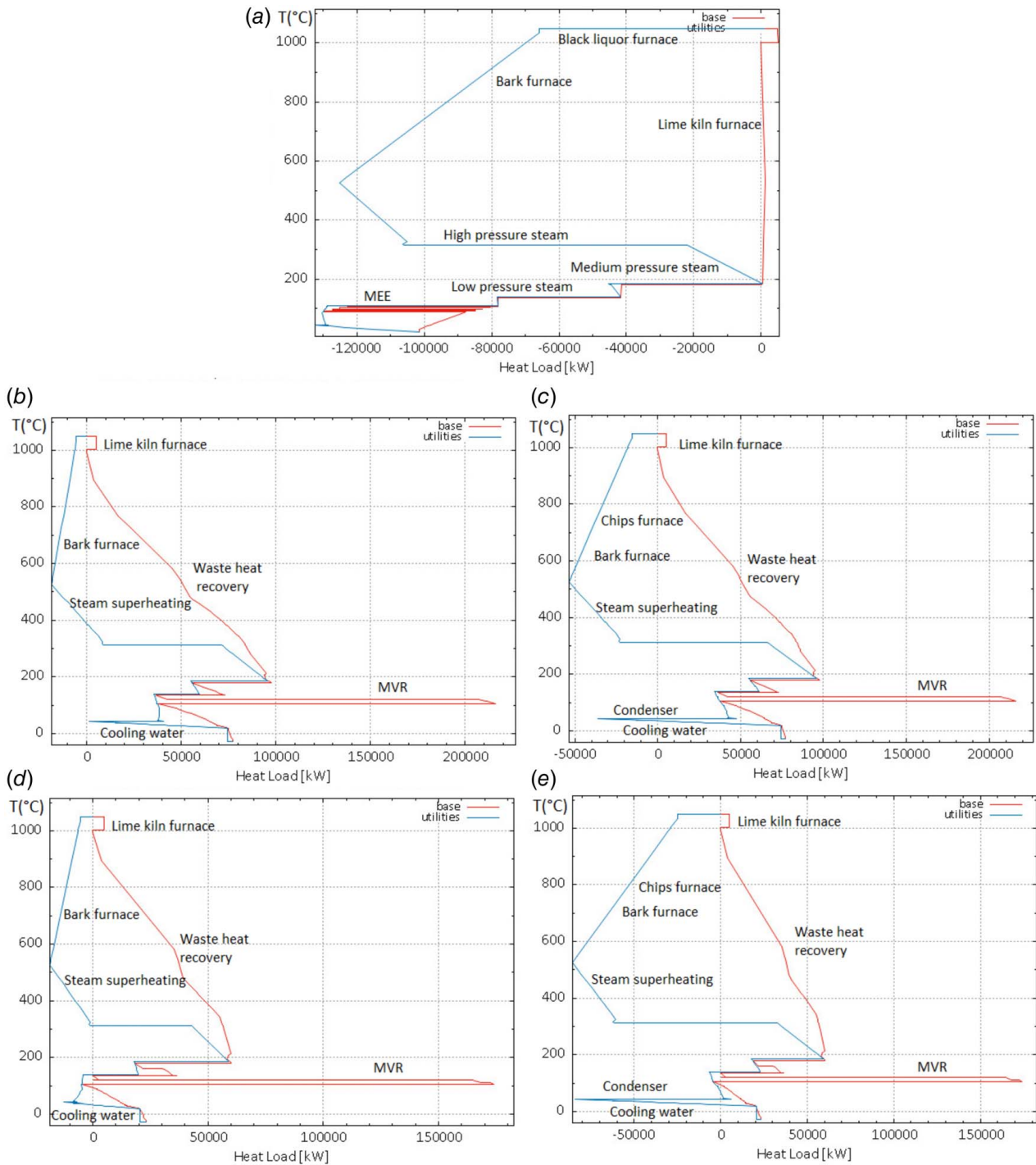
Fig. 4 Integrated composite curves of (a) conventional kraft pulp mill with multiple effect evaporators (four effects). Also, for integrated nitric acid production under (b) mixed or (c) autonomous operating modes; and integrated urea production under (d) mixed or (e) autonomous operating modes (H is the enthalpy flowrate in kW).
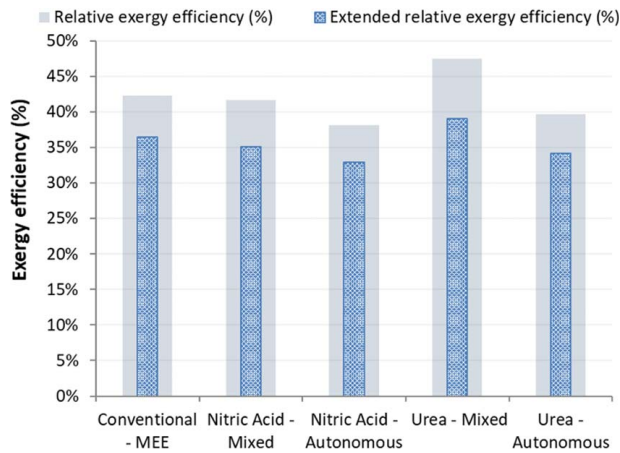
Fig. 5 Relative exergy efficiency for the standalone kraft pulp mill and the integrated chemical production scenarios studied scenarios operating under different modes

In a preliminary analysis, it is assumed that the costs of feedstock and products remain constant. Subsequently, the incremental financial analysis incorporates the uncertainty associated with the costs; thus, simulating the effects of a volatile market. The Monte Carlo method was employed to simulate the stochastic variation of the commodity prices, assuming normal distributions with mean prices (see Table 3) and a standard deviation of 30%.

By considering the lifetime of the integrated pulp and chemical plants, the INPV could be estimated, taking into account the probability of achieving a negative value, referred to as the "likelihood of loss." The "likelihood of loss" is influenced by several factors, including interest rates, market price fluctuations, and carbon taxation. These factors represent risk perception, government subsidies, technology readiness levels, and the impact of inflation over time. For the sake of comparison, three scenarios are evaluated in this study, and the assumptions adopted for the variations in carbon taxes, interest rates, and commodity prices in each scenario are summarized in Table 5.

Results and Discussion

In this section, the performance of the conventional kraft pulp mill with multiple effect evaporators is compared with those of the proposed integrated pulp and chemical plants (nitric acid or urea co-production). The results of the extended exergy analysis are used to demonstrate the effect of biomass conversion integration on the overall performance of the energy systems. Finally, the uncertainty about the prices of the commodities and the cost of the feedstock is analyzed in the light of economic incremental indicators.
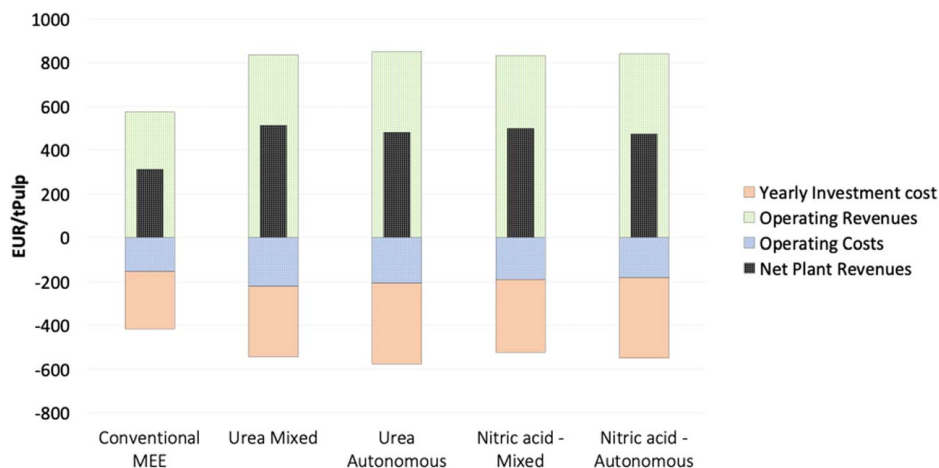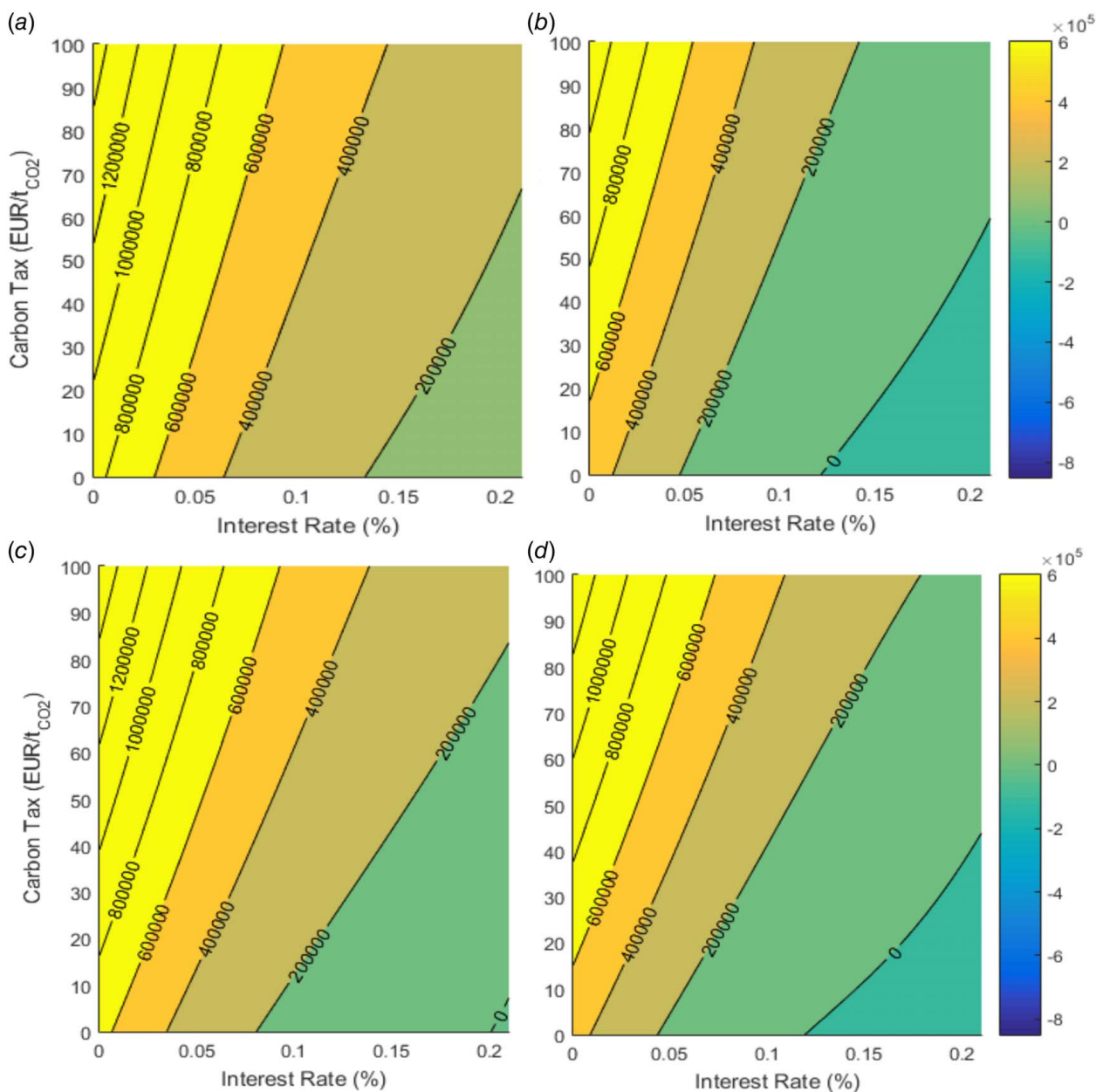

Fig. 6 Yearly investment cost, operating incomes, operating costs, and net revenues of the studied scenarios
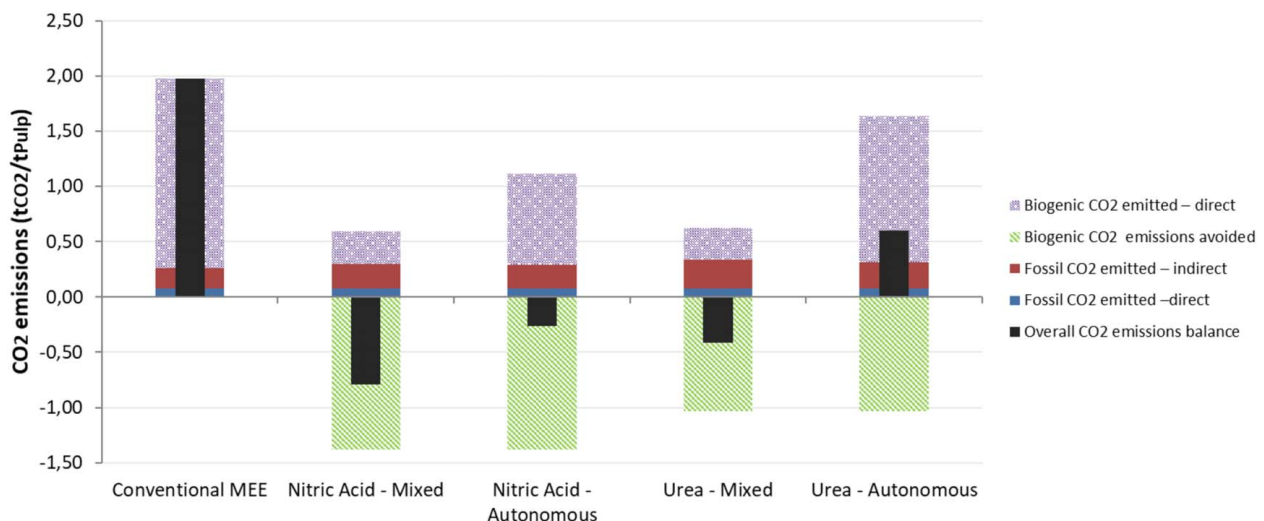
Fig. 7 CO_2 emissions breakdown and balance of the studied scenarios

Fig. 8 Contour plots of INPV (in EUR) for the integrated pulp when co-producing urea under (a) mixed or (b) autonomous operating modes; and nitric acid co-production under (c) mixed or (d) autonomous operating modes

Energy and Exergy Remarks. Table 6 summarizes the exergy consumption remarks of the conventional kraft mill and the integrated plants producing either nitric acid or urea. In this table, the mixed or autonomous operation modes refer to two cases in which there are either intensive electricity or biomass imports, respectively. Thus, in the second operating mode, the cogeneration system of the integrated pulp and chemical production plants is oversized. As can be seen, the overall exergy consumption of the integrated pulp and chemical production plants increases by around 5–28%, compared to the conventional kraft pulp mill. This increase can be attributed to the additional requirements resulting from the energy integration of the alternative facilities into the existing pulping process. In addition, the integrated production routes with nitric acid or urea plants exhibit higher exergy consumption (16–21%) if an *extended exergy consumption* analysis is considered. This analysis is based on the reported exergy efficiency of electricity generation (55.68%) by the

Brazilian electricity grid, as well as the reported exergy efficiencies of the supply chains of oil (95.20%) and biomass (86.13%) [30,31].

In the case of the alternative production routes with nitric acid and urea production, the heating requirements are substantially lower, compared to the standalone kraft pulp mill based on the conventional multiple-effect evaporation system. This fact is a consequence of the enhanced energy integration and the capitalization on the waste heat available in the chemical production steps. In this regard, the cooling requirements also increase in the case of the nitric acid-based solution, which could be further used to supply the heat to a nearby district heating. The marketable CO_2 produced could be also regarded as a source of income for the integrated chemical complexes, with the twofold advantage of its high purity (i.e., coming from the syngas purification unit) and its biogenic origin. This available CO_2 could be even used in CO_2 management systems to store renewable energy from solar [49,50] or

Table 7 Probability that INPV is negative (likelihood of loss in percentage) for scenario DCTIR_SC defined in Table 5, for the co-production of pulp and urea under the mixed operation mode

CO$_2$ tax (EUR/t$_{CO2}$)→	0	10	20	30	40	50	60	70	80	90	100
i (%) 0%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12%	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15%	0.27	0.06	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18%	1.11	0.61	0.17	0.09	0.01	0.00	0.00	0.00	0.00	0.00	0.00
21%	3.47	2.10	0.80	0.27	0.10	0.06	0.00	0.01	0.00	0.00	0.00

Table 8 Probability that INPV is negative (likelihood of loss in percentage) for scenario DCTIR_SC defined in Table 5 for the co-production of pulp and urea under the autonomous operation mode

CO$_2$ tax (EUR/t$_{CO2}$)→	0	10	20	30	40	50	60	70	80	90	100
i (%) 0%	0.10	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3%	0.57	0.21	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6%	5.13	1.79	0.76	0.26	0.04	0.01	0.00	0.00	0.00	0.00	0.00
9%	20.39	11.70	5.86	2.61	0.73	0.29	0.06	0.01	0.00	0.00	0.00
12%	49.27	35.66	22.13	13.90	6.99	3.20	1.56	0.49	0.13	0.10	0.03
15%	74.10	62.74	48.53	35.40	24.06	13.64	8.14	3.93	1.80	0.81	0.24
18%	90.21	82.20	73.27	61.44	49.10	34.89	25.14	15.11	9.23	5.14	2.23
21%	96.03	93.66	87.89	80.44	72.29	58.97	46.56	35.86	24.94	16.01	9.63

Table 9 Probability that INPV is negative (likelihood of loss in percentage) for scenario DCTIR_SC defined in Table 5 for the co-production of pulp and nitric acid under the mixed operation mode

CO$_2$ tax (EUR/t$_{CO2}$)→	0	10	20	30	40	50	60	70	80	90	100
i (%) 0%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6%	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9%	0.51	0.06	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12%	4.10	1.01	0.30	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15%	15.49	6.24	1.93	0.34	0.09	0.00	0.00	0.00	0.00	0.00	0.00
18%	33.74	18.17	7.63	2.61	0.77	0.10	0.03	0.00	0.00	0.00	0.00
21%	54.59	35.46	19.79	9.13	3.89	1.34	0.27	0.03	0.00	0.00	0.00

wind energy after reacting electrolysis-derived hydrogen with the CO$_2$ to produce synthetic natural gas [51].

The integrated composite curves of the conventional and the integrated plants are presented in Fig. 4. In the conventional case (i.e., standalone kraft pulp mill based on multiple effect evaporators), the heating requirements are fully supplied by the combustion of the residual bark and strong black liquor in the recovery boiler. This renders the pulp production system self-sufficient in terms of both steam and power demands, and it even has the potential to export excess electricity. Figures 4(a)–4(e) show the alterations in the integrated composite curves after the installation of an MVR unit. The superheated steam raised using an MVR unit serves the purpose of concentrating the black liquor, leading to a relatively larger extent of heat exchange, at the expense of the consumption of only a fraction of power (due to a high MVR COP >= 10).

Looking at the integrated curves of the integrated chemical production plants (Figs. 4(b)–4(e)), the integrated curves change their shape as soon as the plant is operating either under the mixed mode (i.e., more electricity import) or autonomous mode (i.e., no electricity import). For the autonomous operating modes, a large amount of chips must be burned to balance the energy requirements, resulting in an increased amount of exergy destruction. On the other hand, in the mixed operating modes, the waste heat recovery is maximized due to the import of most of the power consumed in the plant, leading to a reduction of the irreversibility. Clearly, this is

a consequence of the features of the Brazilian electricity mix; thus, it cannot be readily extrapolated to other geographical scenarios. In any case, this is a proof of concept about the need for increasing the efficiency of the energy conversion systems that supply electricity, so that the overall performance of the other economic sectors can be improved.

Moreover, it can be observed from Fig. 5, that there is a significant reduction of the plant-wide exergy efficiency for all the studied scenarios (14% up to 18%) when the extended exergy efficiencies are considered. This is a consequence of the inclusion of additional sources of irreversibility to import biomass and electricity at the gate of the plant.

Additionally, Fig. 6 evidences that the integrated pulp and chemicals production configurations have higher operating revenues, thanks to the value-added products. Even with a higher yearly investment cost of the integrated pulp and fertilizers plants, their net plant revenues are more attractive compared to the conventional kraft pulp mill.

CO$_2$ Emissions Remarks. The direct and indirect CO$_2$ emissions (i.e., related to the supply chains of the electricity, oil, and biomass imports), as well as the overall and net CO$_2$ emissions balance, are shown in Fig. 7. The significant indirect contributions to the overall and net atmospheric CO$_2$ emissions bring to light the

Table 10 Probability that INPV is negative (likelihood of loss in percentage) for scenario DCTIR_SC defined in Table 5 for the co-production of pulp and nitric acid under the autonomous operation mode

CO$_2$ tax (EUR/t$_{CO2}$)→		0	10	20	30	40	50	60	70	80	90	100
i (%)	0%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3%	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	6%	2.06	0.36	0.07	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	9%	12.39	4.44	0.83	0.16	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	12%	39.60	20.50	8.21	2.29	0.51	0.06	0.00	0.00	0.00	0.00	0.00
	15%	69.53	48.99	30.19	12.93	4.76	1.37	0.33	0.07	0.03	0.00	0.00
	18%	87.39	74.31	56.30	36.56	19.67	8.60	2.94	0.83	0.16	0.06	0.00
	21%	95.86	90.26	78.67	63.11	44.10	25.83	12.80	5.31	1.61	0.66	0.09

Table 11 Probability that INPV is negative (likelihood of loss in percentage) as a function of the interest rate for LCT_DIR_SC scenarios defined in Table 5

		Urea mixed	Urea autonomous	Nitric acid mixed	Nitric acid autonomous
i (%)	0%	0.00	0.00	0.00	0.00
	1%	0.00	0.00	0.00	0.00
	2%	0.00	0.00	0.00	0.00
	3%	0.00	0.00	0.00	0.00
	4%	0.00	0.00	0.00	0.00
	5%	0.00	0.00	0.00	0.00
	6%	0.00	0.06	0.00	0.00
	7%	0.00	0.13	0.00	0.01
	8%	0.00	0.69	0.00	0.04
	9%	0.00	1.31	0.00	0.14
	10%	0.00	3.21	0.00	0.66
	11%	0.00	6.84	0.00	1.79
	12%	0.00	12.14	0.01	3.64
	13%	0.00	20.00	0.06	8.64
	14%	0.00	29.10	0.23	14.87
	15%	0.06	39.29	0.69	25.94
	16%	0.03	49.64	1.40	35.74
	17%	0.17	59.49	2.96	46.87
	18%	0.30	68.14	4.81	58.29
	19%	0.56	75.67	8.11	68.79
	20%	0.91	82.19	12.64	77.49
	21%	1.56	86.79	18.50	83.21

Table 12 Probability that INPV is negative (likelihood of loss in percentage) as a function of the interest rate for SCTC_DIR scenarios defined in Table 5

		Urea mixed	Urea autonomous	Nitric acid mixed	Nitric acid autonomous
i (%)	0%	0.00	0.00	0.00	0.00
	1%	0.00	0.00	0.00	0.00
	2%	0.00	0.00	0.00	0.00
	3%	0.00	0.00	0.00	0.00
	4%	0.00	0.00	0.00	0.00
	5%	0.00	0.00	0.00	0.00
	6%	0.00	0.01	0.00	0.00
	7%	0.00	0.03	0.00	0.00
	8%	0.00	0.10	0.00	0.01
	9%	0.00	0.21	0.00	0.00
	10%	0.00	0.73	0.00	0.01
	11%	0.00	1.51	0.00	0.09
	12%	0.00	3.10	0.00	0.16
	13%	0.00	6.07	0.00	0.44
	14%	0.00	10.37	0.00	0.96
	15%	0.01	15.64	0.01	1.84
	16%	0.00	21.86	0.11	3.63
	17%	0.00	29.04	0.14	6.84
	18%	0.07	36.66	0.23	10.07
	19%	0.03	44.04	0.56	14.46
	20%	0.10	53.00	1.01	20.11

environmental issues that may go unnoticed if the imported electricity or biomass is considered as virtually renewable, emission-free inputs. In fact, the large amount of biomass imported, mainly in the autonomous operating mode, proportionally increases the indirect CO$_2$ emissions produced. The avoided CO$_2$ emissions are related to the carbon capture system in the syngas purification section of the ammonia production plant. For the integrated pulp and urea facility, part of this CO$_2$ captured is used to synthesize urea; thus, impacting the overall CO$_2$ emissions balance. Clearly, as soon as the urea is used in the soil, it releases the CO$_2$ back to the atmosphere. On the other hand, negative CO$_2$ emissions in the nitric acid production represent an opportunity for issuing carbon credits and, thus, increasing the financial attractiveness of the integrated chemical system.

If the direct biomass-derived emissions are considered as neutral (i.e., circular) emissions, all the integrated setups achieve net negative CO$_2$ emissions values: between -1.08 t$_{CO2}$/t$_{PULP}$ and -1.09 t$_{CO2}$/t$_{PULP}$ for the nitric acid co-production plant operating under the mixed and autonomous modes, respectively; and -0.70 t$_{CO2}$/t$_{Pulp}$ and -0.72 t$_{CO2}$/t$_{Pulp}$ for the urea co-production plant operating under the mixed and autonomous modes, respectively. The negative values indicate an overall positive impact toward the depletion of the CO$_2$ present in the atmosphere.

According to Fig. 8, an extensive import from a highly renewable electricity mix brings about positive values of INPV regardless of the carbon tax and the chemical production route. The economic results for the pulp and urea co-production route are shown in Fig. 8(*a*), while plots presented in Fig. 8(*c*) are for the pulp and nitric acid co-production routes. These results contrast with the performance of the co-production routes based on the autonomous operation mode, in which the inefficient combined heat and power generation in the cogeneration plants (without electricity import) may lead to conditions of negative INPV, especially for low carbon taxes and high-interest rates. Meanwhile, in the case of the autonomous operating mode, interest rates above 13% do not favor any more positive INPVs. Certainly, carbon pricing could be a measure for pushing the economic transformation and improve the waste recovery, but the effects of its application must be carefully evaluated as it can have a strong effect on the assets and their economic feasibility [52].

The heat maps given in Tables 7–10 summarize the results for the scenario (i) DCTIR_SC defined in Table 5. For the urea (Tables 7 and 8) and the nitric acid (Tables 9 and 10) co-production routes, the results suggest favorable scenarios for both operation modes (mixed and autonomous), as positive INPVs are likely probably to be obtained for almost all the range of carbon taxes evaluated, but still depending on the interest rates.

Meanwhile, the heat maps shown in Tables 11 and 12 summarize the results for scenarios (ii) LCT_DIR_SC and (iii) SCTC_DIR, respectively, defined in Table 5. As it can be seen, the integrated pulp and chemical fertilizers plants show more favorable results

in terms of likelihood of loss by operating under the mixed operation mode. This fact advocates for the fertilizers co-production in scenarios with a diversified energy matrix based on renewable resources, with electricity mixes mainly relying on renewable resources. Undoubtedly, carbon pricing along with broader fiscal reforms will be necessary to drive a sustainable transition that could lead to the achievement of short-term and long-term net zero goals [52].

Conclusions

In this work, the advantage of the energy integration of a kraft pulp mill and fertilizers production plants (i.e., nitric acid or urea) via black liquor gasification process is compared to the performance of a conventional kraft pulp mill. The accounting of the extended exergy consumption and the extended exergy efficiency of the upstream supply chains allowed to assess the cradle-to-gate impact of the integrated pulp and chemical production routes. An increase between 16% and 21% in overall exergy consumption was observed when these supply chain inefficiencies are considered. The integrated composite curves of the integrated pulp and chemical plants were compared to the curves of the standalone conventional kraft pulp mill, which suggested potential improvements and also challenges in terms of exergy destruction and waste heat recovery. Two different operating modes (mixed and autonomous modes) can impact waste heat recovery. The overall emissions balance was found to be as much as 1.97 t_{CO_2}/t_{Pulp} for the conventional kraft pulp mill; whereas for the integrated pulp and urea or pulp and nitric acid co-production plants, this balance varied from -0.79 t_{CO2}/t_{Pulp} to 0.60 t_{CO2}/t_{Pulp}. Despite the increased investment cost, the operating revenues of the alternative configurations are not considerably impacted in comparison with the conventional kraft pulp mill, due to the commercialization of the newly produced value-added CO_2 and fertilizers. In any case, the results proved to be strongly dependent on the indirect emissions, the energy resources consumed (e.g., chips or electricity) and the market prices adopted for the resources and the products of the integrated plants. Finally, the incremental financial analysis under uncertainty of the feedstock costs and carbon taxes allowed to understand the behavior of the integrated systems proposed by considering different market fluctuations. As a result, for the nitric acid and the urea production, positive INPVs are likely in most of the range of carbon taxes considered, provided that a mixed import of biomass and electricity is accomplished. In fact, even when the systems are subject to linear-increasing or stochastic carbon taxes, the scenarios operating under the mixed mode (intensive electricity import) showed a larger potential for decarbonizing the pulp and fertilizer sector with a more robust economic performance.

Conflict of Interest

There are no conflicts of interest.

Data Availability Statement

The datasets generated and supporting the findings of this article are obtainable from the corresponding author upon reasonable request.

Nomenclature

f = load factor
q = heating or cooling duty from utility systems (kW)
r = indirect CO_2 emissions factor (g_{CO_2}/kJ_{fuel})
y = existence optimization factor
B = specific chemical exergy (kJ/kg)
B = chemical exergy (kW)
C = carbon mass fraction (%)
H = hydrogen mass fraction (%)
M = molecular weight (kg/kmol)
N = number of utility unit or temperature intervals
R = cascaded heat (kW)
T = temperature (°C)
W = power (kW)
FC = fixed carbon (%)
LHV = lower heating value (MJ/kg)

Greek Symbols

φ = ratio of the chemical exergy to the lower heating value
ω = process or utility unit

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