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Techno-economic and environmental analysis of high temperature heat pumps integration into industrial processes: the ammonia plant and pulp mill cases

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ABSTRACT

Heat pumps will play an important role in improving the performance of the industrial processes aiming to decarbonize their heating requirements. Yet, defining the best operating conditions of those devices may be a challenging task, as they are embedded in larger energy conversion systems and in direct competition with fired and electric heaters and other waste heat recovery systems. The costs of the energy inputs also influence the selection of either a heat pump or a gas boiler, which affects the overall efficiency and the incremental cost of the final solution. Thus, a systematic analysis must be applied in order to determine the best option to supply the heating requirement, without considerably impacting the operational feasibility of the overall plant. In this work, the base-case performance of two industrial applications with intensive heating demand, namely, the solvent regeneration process of a carbon capture unit and the black liquor concentration process of a kraft pulp mill, are compared to that of the scenarios in which a high temperature heat pump or a mechanical vapor recompression unit are integrated, aiming to reduce the energy consumption and the environmental impact. The benefits of the integration of a heat pump or a mechanical vapor recompression unit over a conventional reboiler and a multiple effect evaporation system are discussed in the light of thermodynamic, economic and environmental indicators. As a result, the alternative approaches remain competitive vis-à-vis the conventional solutions in terms of energy consumption and operating costs. In addition, the emissions associated to the heating applications could be reduced by 45% if a high temperature heat pump is integrated. The optimized solution using a heat pump has an overall exergy efficiency 9% higher compared to the typical configuration of the ammonia plant. In pulp mills, the integration of mechanical vapor recompression systems slightly affects the performance compared to the conventional scenario with a multiple effect evaporation system.

Introduction

Heating is pervasive in industrial and chemical applications, including disinfection, distillation, drying, regeneration, among other uses. Hot utility streams with temperatures ranging from 60 °C to 140 °C are required to supply the heating demands in the fertilizers, pulp and paper, and food production sectors. The heating process is typically provided by burning fossil fuels, which hinders the efforts to decarbonize those industrial activities. On the other hand, waste heat is an abundant byproduct in those facilities, as it is derived from the exothermic chemical reactions occurring throughout the industrial and chemical plants. Despite its residual energy content, the low-grade waste heat is normally released to environment, increasing both the cooling duty and energy consumption of the system. In this regard, heat pumps could be used to upgrade the waste heat available at low temperature and provide the heating demands, while partially or totally replacing the fired boilers; thus, minimizing the environmental impact [1]. Unlike the electric resistances, which degrade power into thermal energy; most of the energy input to the heat pump is waste heat, which results in a simultaneous reduction in the cooling duty and the electricity import. The potential of application for the heat pump systems in the industry is significant, especially when envisaging more stringent environmental regulations and volatile fuel prices. According to the International Energy Agency report *Net Zero by 2050: A roadmap for the global energy*

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sector, heat pumps could cover 15 % of process heating demand of light industries by 2030, and this share may increase to 30 % by 2050 [2]. The use of high temperature heat pumps has been proposed to increase the efficiency [3] and abate the atmospheric emissions in different energy conversion systems [4]. In fact, an effective deployment of heat pumping technology may reportedly reduce by 35 % the CO_2 emissions in heating applications [5]. High temperature heat pumps (HTHP) have been the subject of various studies [6,7] aiming to improve and disseminate the knowledge about their research status, market overview and future developments of HTHPs. Collaborative tasks have been conducted within the IEA Technology Collaboration Programme on Heat Pumping Technologies (TCP HPT) to promote the information exchange and the development and implementation of this technology [8,9]. Challenges related to the need for larger temperature lifts and higher supply temperatures [6,8], along with better refrigerants with low global warming potential (GWP), have been identified [5–8]. Enhanced reliability and safety of the existing compressor technologies for the large heating capacities (>1 MW) have been also spotlighted [6].

Studies on the energy integration of industrial heat pumps

An extensive review of high temperature heat pump systems (>90 °C) has identified several application opportunities particularly in the food, paper, metal and chemical industries, for heating capacities ranging from 20 kW up to 20 MW. Most cycles are single-staged and differ in the compressor type and refrigerant used (e.g. R245fa, R717, R744, R134a or R1234ze(E)). Temperature lifts between 95 K and 40 K entail coefficients of performance varying from 2.4 to 5.8 [7]. More recently, an study on the electrification of the U.S. manufacturing sector aimed to identify and generalize the potential applications of industrial heat pumps [10]. However, over-conservative assumptions and generalizations, such as the temperature conditions of the heat sources, have led to misleading conclusions about future electricity demands and marginal costs. According to the authors, it is advisable to explore suitable waste heat sources at higher temperatures to minimize the temperature lifts, and consequently the electricity costs.

The integration of HTHPs (160 °C) has been proposed to supply the heating demand to a brick drying process (400 kW), achieving coefficients of performance (COP) between 4.6 and 2.6 for temperature lifts ranging from 40 K to 75 K, respectively [11]. The pulp industry has also advocated for the integration of HTHPs (~200 °C) in the drying processes in order to achieve net-zero CO_2 emissions goals; although an study suggested that HTHP integration may increase the energy related costs by 49 %, compared to the conventional scenario [12]. Meanwhile, the installation of a 4 MW HTHP in the drying section of a pulp mill, which recovers waste heat at 50 °C to produce hot water at 70 °C for a nearby district heating system (3000 dwellings), has reportedly reduced the overall energy consumption of the pulp mill [10]. Large heat pumps (4 MW, COP ~ 11) can be also integrated to paper mills to recover waste heat from the boiler stack [3]. In a dairy plant, the integration of a HTHP (>100 °C, T lift of 50 K) has been proposed to upgrade the waste heat from cleaning water to supply the heating requirements to the milk pasteurization unit [13]. The energy integration of heat pump systems in food drying applications (500 kW − 3 MW) could allow reducing by 60 % the energy consumption by recovering the condensation enthalpy of the moist air. A thorough review on the advances in heat pump-assisted drying technologies and its industrial applications can be found in [14]. In ammonia plants, a mechanical vapor recompression system [15] has been proposed as an alternative to other heat recovery systems at low temperature, such as feedstock and boiler feedwater preheating [4]. Industrial heat pumps applications also include water desalinization to produce hydrogen via water electrolysis [16] and regeneration of temperature swing adsorption (TSA) units for the biogas purification (110–125 °C) [17]. Utility water heating for cleaning purposes, process bath heating, drying, and thermal preservation processes have been also identified as suitable processes that can be supplied with the market-available heat pump technologies [18]. As for Swiss pulp, food and beverage sectors, a techno-economic bottom-up cost optimization model reported no cost-optimal operation of a HTHP running above 150 °C, due to the high temperature lifts. Incentivizing the exploitation of the large waste heat recovery potential in the Swiss industry may require high CO_2 prices (400 EUR/t_{CO2}) and additional policies to overcome the deployment barriers by supporting investment and flexible system-serving operation of the heat pumps [19].

Despite the relevance of the previous works, none of them has analyzed the impact of integrating HTHPs in fertilizers or pulp production plants under different scenarios of carbon taxation and variable costs of the energy inputs. The previous studies also focused on the implementation of HTHPs without considering the constraints imposed by the pinch analysis to the entire energy system. As a consequence, the integration of the HTHP may become counterproductive and increase the overall energy requirement. The interaction and competition of the HTHP with the existing heating appliances also bring more complexity to the heat pump design, integration and optimization problem. Accordingly, in this work, thermodynamic and computational methods are used to elucidate potential gains of integrating high temperature heat pumps into a syngas purification unit of an ammonia plant and a black liquor concentration process in a pulp mill, considering the impact of the carbon tax and the variable costs of the energy inputs. A rigorous mixed integer linear programming (MILP) approach is used to define the most suitable scenarios for activating the HTHPs and the most interesting temperatures to integrate these devices into those industrial applications, which together are responsible for about 8 % of the global energy consumption and 4 % of the industrial CO_2 emissions [20,21].

Methods

This study considers the heating and cooling requirements of the entire energy systems, thus the maximum potential for waste heat recovery through all the operation units is accounted for to reduce the net energy import. To this end, combined energy integration and exergy methods are applied, whereas computational visualization and optimization tools guarantee a correct sizing and integration of high temperature heat pumps to the industrial plants. The operating conditions of the ammonia and the pulp production plants are firstly described, along with the characteristics of the utility units that must supply the heating and cooling demands. Finally, an optimization problem based on maximization of operating revenues is stated to determine the best arrangement and operating conditions of the utility systems. Various indicators are defined to rationally compare the most suitable solution for heating applications, including economic, thermodynamic, and environmental aspects.

The modelling and simulation of the multicomponent, multiphase systems in complex chemical processes is performed using Aspen Plus® [22] software, incorporating the semi-empirical equations of state (EoS) of Peng-Robinson with Boston-Mathias (PR-BM) modifications, and the Redlich-Kwong (SRK) EoS with Soave modifications. For modelling the chemical absorption carbon capture system, Electrolytic Non-Random Two Liquid (ENRTL-RK) method is employed to account for strongly non-ideal liquid properties, Henry components, and dissociation chemistry inherent to the reactive absorption–desorption processes. The properties of water are calculated using Coolprop software [23], based on the IAPWS 95 formulation. Meanwhile, the utility systems are modeled via equation-oriented subroutines in the Lua programming language. Additional equations for the mass and energy balances of the utility units are setup to reflect the interactions between the whole set of energy technologies.

Process parameters of the ammonia production plant

As it is shown in Fig. 1, the syngas and ammonia plants comprise a syngas production section with a saturator, a pre-reformer, the primary and secondary reformers, and the water gas shift reactors. Saturated

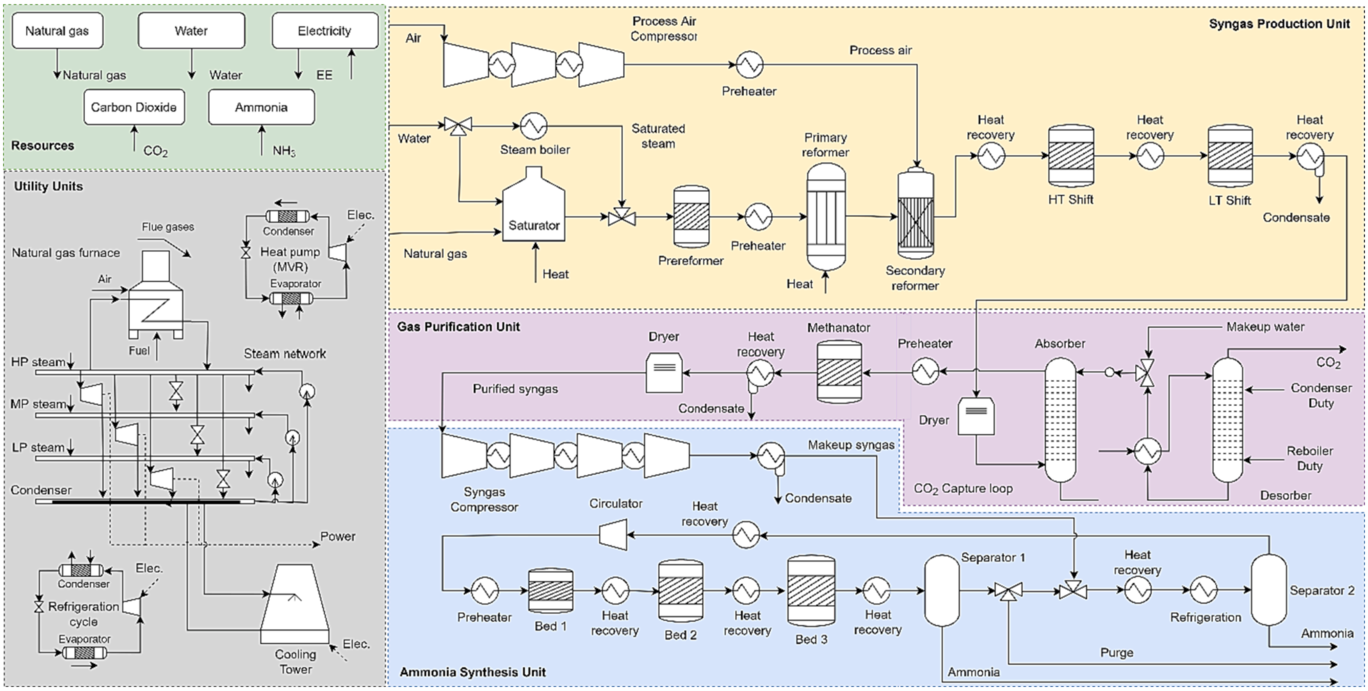

Fig. 1. Conventional ammonia production plant and the set of utility systems that can be integrated, including a high temperature heat pump.

natural gas feedstock goes into an adiabatic pre-reformer, wherein reactions (R.1-R.2) occur at milder temperatures (<500 °C) to convert heavier hydrocarbons and, thus, reduce the energy demand of the primary reformer furnace [24]. In the primary reformer, natural gas feedstock reacts with process steam at a steam-to-carbon ratio (S/C) typically above 2.5. Favorable conditions for reduced methane slip involve high temperatures (>790 °C), moderate pressures (30 bar), as well as a relatively high steam-to-carbon ratio. These conditions prevent formation of carbon deposits on the catalyst. In order to introduce the nitrogen required for the downstream ammonia production (N_2:H_2 = 1:3 M), a secondary reformer is employed. In this unit, the reformed mixture is partially burnt with air to provide the necessary stoichiometry and maintain the heat balance. One third of the total power consumption in the plant is allocated to the compression of process air [25].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^o_{298} = 206\ kJ\ mol^{-1} \tag{R1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^o_{298} = -41\ kJ\ mol^{-1} \tag{R2}$$

The effluent from the secondary reformer is cooled to the suitable temperatures for the subsequent high and low-temperature water gas shift reactors (350/200 °C), which increase the production of hydrogen at the expense of the carbon monoxide and water content in the reformed gas (R.2) [26]. The shifted gas is cooled and the excess water is separated previously to the removal of the CO_2 from the syngas using chemical absorption agents, like di-ethanol amine (DEA). In this system, the flue gas is contacted in an absorption column with a selective solvent designed to remove up to 99 % of CO_2. Next, the hot rich amine enters a desorption column, where low-pressure steam (sat. 3 bar, 3.5 MJ/kg_{CO2}) is consumed in the reboiler to regenerate the solvent and strip out the CO_2 absorbed [27]. The hot lean solvent is cooled and pumped back to restart the loop, whereas the CO_2 desorbed is released overhead, conditioned and marketed for further applications. To avoid corrosion issues, the acid gas loading and amine solution concentration should be limited to 0.40 $kmol_{CO2}/kmol_{DEA}$ and 35 %wt., respectively. Carbon oxides content (0.32 % mol CO and 600 ppm CO_2) after the CO_2 capture unit may degrade the ammonia catalyst, thus, a portion of the produced hydrogen is consumed to convert them into inert methane in a methanator (reverse R.1).

Next, syngas is compressed up to 150–200 bar and fed to an ammonia synthesis loop (R.3), which is composed of a series of highly exothermic reactor beds with intercooling. In order to enhance the nitrogen conversion per pass (10–30 %), the inlet temperature into each catalytic bed is controlled by a cooling process that extracts waste heat between 300 °C and 500 °C, typically generating medium pressure steam [28]. After the reactor, most of the ammonia is separated by condensation from the unreacted mixture using cooling water. Yet, since complete ammonia condensation cannot be achieved through water or air cooling alone, the ammonia-rich gas is refrigerated, bringing its temperature down to −20 °C via a vapor compression refrigeration system. Finally, to prevent the buildup of inerts (Ar, CH_4), a continuous withdrawal of a portion of the unreacted hydrogen-nitrogen recycled mixture is carried out after the removal of ammonia and right before the introduction of fresh syngas.

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \Delta H^o_{298} = -92\ kJ\ mol^{-1} \tag{R3}$$

Since ammonia plant components are intricately interconnected, any changes in one section can impact the global operation, particularly affecting the overall heat and power balances of the plant. Although a large portion of the waste heat available throughout the chemical plant is recoverable to generate power and reduce the fuel import, combined heat and power production is a relatively inefficient energy conversion process. As a consequence, the steam network is generally oversized, leading to an increase of condensation losses and higher environmental impact associated to the fertilizers production. This fact points towards the potential integration of a HTHP to supply the process heat in a more efficient way.

Process parameters of the pulp production mill

Other interesting application for the high temperature heat pumps is the drying process of black liquor, which is a byproduct of pulp production in the kraft pulp mills. Fig. 2a illustrates the layout of a conventional mill, in which the wood goes through a debarking and chipping process, and the bark is sent to a biomass furnace. Debarked wood is fed to a digester (145–180 °C), along with a strong alkaline solution called white liquor (60 % NaOH, 25 % Na_2S, and 15 % Na_2CO_3),

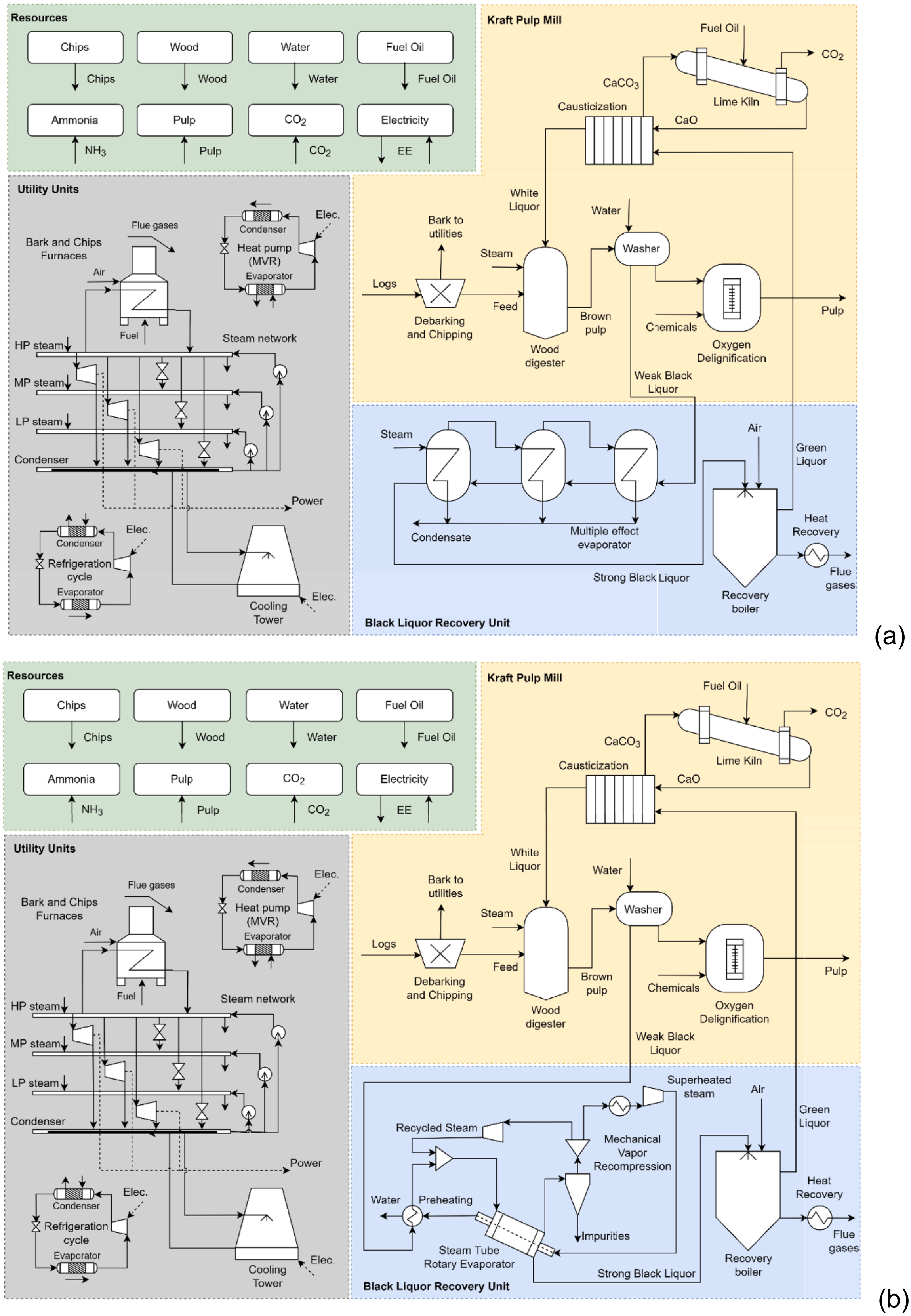

Fig. 2. Kraft pulp mill with (a) multiple effect evaporators and (b) a mechanical vapor recompression system.

that helps separating the cellulose from the lignin [29]. After a washing and an oxygen delignification processes, the pulp is dried to about 10 % wt. of moisture and sold to the market or used to produce paper. In this work, a pulp yield of 46.51 %wt. with respect to the total amount of digested biomass is assumed [30]. The byproduct of the digestion process, known as black liquor, consists of a weak solution of dissolved chemicals and lignin separated from the cellulose (1.44 t_{BL}/t_{pulp}) [30]. This residue retains almost 50 % of the energy initially embodied in the wood [31], therefore it is usually concentrated (>80 % wt. solids) and burned in the recovery boiler to generate steam. The smelt derived (green liquor) is recovered and recycled to a causticization process, where it reacts with lime to convert the sodium carbonate into sodium hydroxide and to produce the white liquor used again in the digester [32]. The precipitated calcium carbonate is sent to a lime kiln and heated to recover the calcium oxide by consuming fuel oil. In this work, the power and steam demands are adapted to produce about 880 air dried tons of pulp per day [33,34].

The concentration process of black liquor is typically handled by multiple effect evaporators (85 %wt. solids), although it is also possible to use mechanical vapor recompression systems for this purpose (Fig. 2b). A mechanical vapor recompression unit (MVR) uses power to superheat the steam separated, thus avoiding the excessive steam generation in boilers, and the subsequent condensation losses [35]. In this regard, the combined integration of a cogeneration system and a heat pump technology poses an interesting trade-off between electricity import and combined heat and power generation. There is also the possibility of exporting electricity to the grid after satisfying the internal electricity demands, including those of the ancillary energy technologies represented in Fig. 2a-b, namely, the refrigeration and cooling water systems.

While electricity consumption may play a decisive role in decarbonizing the heat supply to industrial applications usually based on fossil energy resources; the electrification of the heating processes, e.g. using HTHPs, may radically change the shape of the composite curves of the integrated chemical plants. In fact, by shifting from a typical solution with combined power and heat production to a mixed operating mode with intensive electricity import, different energy technologies and operating conditions may prevail over the business-as-usual scenario. Also, the upgrade of the waste heat streams into high-grade utility streams adds more complexity to the energy balance of the utility systems. In view of the clashing solutions and different sizing and installation options, a systematic analysis becomes necessary to elucidate the best options to deliver the heating and cooling requirements with the minimum operating costs. In the following sections, the technical parameters used for modelling and simulating the utility units, proposed for supplying the energy demands of the chemical plants, are discussed.

Modelling and simulation of the utility units

The modelling and simulation of the utility units is performed using an equation-oriented approach in Lua programming language. The technical parameters of the main components of the utility systems are presented next, including those related to the high temperature heat pumps.

Natural gas, biomass and black liquor furnaces

The integration of fossil or biomass-fired furnaces may still be necessary to provide the heating requirements at very high temperatures that cannot be attained using high temperature heat pumps. In the ammonia plant, natural gas is used not only as a feedstock, but also as a fuel. In that plant, the heat recovery convection train (HRCT) of the gas-fired reforming furnace guarantees the heat balance of the remaining processes, after satisfying the energy needs of the primary reforming reaction (~790 °C). The CO_2 desorption processes in the syngas purification unit (~120 °C) and the combined heat and power production in the steam network (<300 °C) are examples of processes that typically depend on the HRCT. For modelling the natural gas-fired furnace, the lower heating value of natural gas is assumed as 50 MJ/kg, and the combustion achieves an adiabatic flame temperature of 1950 °C. Minimum stack temperature of 150 °C is considered at the outlet of the HRCT [36]. Meanwhile, the recuperation of the chemical energy of the black liquor can be achieved in a Tomlinson recovery boiler; which entails less additional fuel consumption (e.g. chips) to balance the pulp mill demands. The biomass furnace is modeled considering an adiabatic flame temperature of 1350 °C and a lower heating value of 11.3 MJ/kg for 40 %wt. moist biomass fuel. The stoichiometric air-to-fuel mass ratio is set as 3.98 and the excess air is set as 20 %. Finally, to model the black liquor combustion in the recovery boiler (LHV: 10.2 MJ/kg), an adiabatic flame temperature of 1740 °C is adopted [37]. These parameters, along with other optimization variables, such as the fuel mass flow rate, the excess air ratio and the combustion air preheating temperature, can be used to characterize the performance of the furnaces, including their stack losses. It is worthy to emphasize that waste heat is also available from other energy conversion processes, such as the exothermic reactors (e.g. methanation, ammonia synthesis, water gas shift), which can generate excess heat as to satisfy an important part of the energy requirements of the chemical plants. For this reason, a plant-wide energy integration analysis is necessary to elucidate the minimum energy requirement and the optimal size of the furnace technologies, when they are competing with heat pumping energy systems.

Steam network superstructure

The steam network is modeled as a superstructure composed of steam generation drums at different pressure levels connected by headers, with the possibility of expanding steam through one or more steam turbines, letdown valves or even steam bleedings from either backpressure or extraction-condensing steam turbines (see Figure 1 and 2). The water properties are calculated using Lua Coolprop library [38]. The pressure levels are selected based on the shape of the Grand composite curve determined for the chemical processes. For instance, knowing the waste heat availability throughout the chemical plant and the temperature levels thereof, a high pressure (HP) steam generation unit can be enabled for cogeneration purposes (>100 bar). Meanwhile, the steam required by the process units, such as the reforming, shift and digestion reactors could be supplied either by medium pressure (MP) steam generators (12–30 bar), steam throttled from higher pressure levels, or more efficiently, by a partial extraction of steam turbines. Low pressure steam required in the CO_2 desorption unit or in the pulp treatment process could be either generated at low pressure or extracted from a steam turbine (~3 bar). Finally, depending on the overall energy balance, a steam condensation level (<0.7 bar) could be adopted as to increase the power generation in an extraction-condensing steam turbine. The corresponding pumping systems and other devices for steam (de)superheating, boiler feedwater preheating, mixing and deaeration may be also included. Further details on the proposed steam network superstructure can be found elsewhere [4,39].

Cooling water and refrigeration systems

Cooling water provides the cooling duty to both processes and utility systems, and its optimal operation helps reducing the use of costly refrigeration units. The cooling water unit is modeled based on the water supply and return temperatures (15 °C/30 °C) equivalent to an enthalpy change of 62.8 kJ/kg_{water}. The wet bulb temperature, the range ($T_{return}-T_{supply}$) and the approach ($T_{supply}-T_{wetbulb}$) temperature differences are determined considering 40 % relative humidity [40,41]. A specific electricity consumption of 0.021 kW_{ee} per kW_{th} is used to estimate the energy consumption of the cooling tower [4]. On the other hand, the refrigeration unit is crucial for operating chemical sections, such as the ammonia synthesis loop, as the cooling water alone is not satisfactory to fully condense out ammonia from the unreacted mixture. An ammonia (R717) vapor compression refrigeration system is adopted to supply the cooling duty in the ammonia loop (-20 °C). The model of the refrigeration system considers an estimated Second Law efficiency of $\varepsilon = COP_{actual}/COP_{carnot} = 0.45$ [7], which is the ratio of the Coefficient of Performance of the actual system (COP_{actual}) to the ideal Carnot COP. The Carnot COP is turn a function of the evaporation (T_{evap}) and condensation (T_{cond}) temperatures of the refrigeration cycle ($COP_{carnot} = T_{evap}/\Delta T_{lift}$ where $\Delta T_{lift} = T_{cond} - T_{evap}$). The condensation temperature and the temperature lift are chosen to minimize the excess power consumption and, thus, the waste heat produced below the pinch point. The condenser waste heat can be upgraded and used to supply heat to other processes, otherwise it needs to be rejected to the cooling water system.

Mechanical vapor recompression system

Mechanical vapor recompression (MVR) systems can be open and semi-open setups. In the former type, vapor is heated by recompression and used as the direct heating medium using its condensation enthalpy [42]. Semi-open systems transfer heat indirectly to the process via heat exchangers. MVRs are typically designed for water (R-718) as working fluid and often achieve higher COPs (>10) due to their reduced temperature lift [9]. Alternative drying units, based on mechanical vapor recompression (MVR) systems (Fig. 2b), have been proposed to replace the multiple effect evaporators (MEE) commonly used in the conventional kraft pulp mills (Fig. 2a) [43]. Firstly, the black liquor is preheated; next, it enters a rotary tube evaporator, wherein the countercurrent heat exchange with the superheated steam increases the black liquor solid content up to 85 %wt. The evaporation temperature (120 °C) is correlated to the concept of equilibrium moisture content ($MC_{eq} = 54.68\ e^{-0.046T}$) [44,45]. Heavy black liquor leaves the evaporator, whereas the extracted moisture is split into two streams: a recycled and a purged steam. The former stream is recirculated to the evaporator to improve the heat transfer inside the rotary drier, while the purged stream is recompressed and superheated to supply the evaporation heat. As the use of electrical energy replaces the production of a large amount of saturated steam in steam boilers and a large part of the condensation energy of the produced vapor can be recuperated, the equipment can be more compact and the condensation energy losses can be minimized. The water vapor recompression systems are operated using large compressors or high-speed oil-free turbo compressors with high flow rate and low-pressure ratio in order to compensate for the low density of the water vapor [7].

Heat pump systems

A heat pump (HP) is a device designed to transfer heat from lower to higher temperatures, while consuming electrical energy. A heat pump reclaims and upgrade otherwise wasted heat for practical use. HPs typically rely on the vapor compression principle, which can be done in single or multiple stages with intercooling. Unlike conventional heat pumps, the high-temperature variants employ modified components and new working fluids to enhance the efficiency of the heating supply at elevated temperatures (>100 °C). Ammonia-based (R-717) heat pumps featuring cast steel compressors withstand pressures up to 76 bar and 110 °C. Hydrocarbons refrigerants with very low global warming potential (GWP), like n-butane (R-600) and pentane (R-601), exhibit higher critical temperatures of 152 °C and 196.6 °C at 38.0 bar and 33.7 bar, respectively. R-600 is deemed suitable for HTHPs with condensation temperatures up to 120 °C. R-1336mzz(Z) has a high critical temperature of 171.3 °C at a relatively low pressure of 29 bar and can supply heat at sink temperatures of 160 °C. As for the compressor selection, on the one hand, screw compressors with a pressure ratio of 20 can be used for up to 8 MW of heating capacity, allowing for a more compact design; however, an oil management system is required due to potential oil degradation at elevated temperatures. On the other hand, turbo compressors offer advantages such as small space requirements, large flow rates, good speed control, and low abrasion. However, they also feature lower pressure ratios per stage. In comparison to the mechanical vapor recompression (MVRs) systems, which generally exhibit higher Lorentz efficiencies (0.45–0.91), heat pump efficiencies are slightly lower (0.35–0.59), which entails the need for a specific strategy to effectively integrate the heat pump systems into chemical applications [9]. Thus, a thorough inspection of the process Grand composite curve is necessary in order to determine whether a heat pump is competitive vis-à-vis other heating options. Temperature lifts directly influence the performance and the arrangement of the heat pumping systems, as it will be discussed [9].

Optimization problem definition

Due to the possibility of importing or producing electricity at the expense of the reduction or increase of the fuel consumption, a trade-off between the additional fuel and electricity imports arises as the optimal utility systems are targeted. In other words, the new utility demands, triggered by the shift to alternative production routes, may lead to completely different integration approaches between the chemical units and the utility systems. For this reason, the OSMOSE Lua platform [46] is employed to calculate the minimum energy requirements (MER) of the chemical plants. Subsequently, this framework handles the mixed integer linear programming (MILP) problem that works out the best arrangement of energy technologies and their operating conditions, so that the operating costs are minimized. Aspen Plus® software is used to simulate the chemical plants and to transfer data to OSMOSE Lua to build the MILP problem described in Eqs. (1–3). In this way, the integer variables, y_w, related to the existence or absence of any utility unit ω and its respective continuous load factor, f_w, can be determined by minimizing the objective function given in Eq. (1):

$$\min_{f_\omega,\ y_\omega\ R_r, W} \left[\begin{array}{l} f_{Chips\ Biomass}(B\cdot c)_{Chips\ Biomass} + f_{Wood\ Biomass}(B\cdot c)_{Wood\ Biomass} + f_{Natural\ Gas}(B\cdot c)_{Natural\ Gas} + f_{Oil}(B\cdot c)_{Oil} \pm f_{Elec\ Grid}(W\cdot c)_{Elec\ Grid} \\ + f_{CO_2\ Taxed}(m\cdot c)_{CO_2 Taxed} + \dfrac{Z_{HP\ or\ MVR} \times Ann\_factor}{8760} - f_{Pulp}(B\cdot c)_{Pulp} - f_{Ammonia}(B\cdot c)_{Ammonia} - f_{CO_2\ Marketed}(m\cdot c)_{CO_2\ Marketed} \end{array} \right] \quad (1)$$

Subject to:

- The heat balance at the temperature interval *r,* and the produced and consumed power balance:

$$\sum_{\omega=1}^{N_\omega} f_\omega q_{\omega,r} + \sum_{i=1}^{N} Q_{i,r} + R_{r+1} - R_r = 0 \quad \forall r = 1\ ..\ N \ and \ \sum_{\omega=1}^{N_\omega} f_\omega W_\omega + \sum_{chemical\ units} W_{net} + W_{imp} - W_{\exp} = 0 \quad (2)$$

- The utility units existence, load and solution feasibility conditions:

$$f_{\min,\omega} y_\omega \leqslant f_\omega \leqslant f_{\max,\omega} y_\omega \quad \forall \omega = 1\ ..\ N_\omega \ and \ R_1 = 0,\ R_{N+1} = 0,\ R_r \geqslant 0 \ and \ W_{imp} \geqslant 0,\ W_{\exp} \geqslant 0 \quad (3)$$

where, N is the number of intervals of temperature, based on the supply and the target temperatures of the various heat streams; Q is the heat exchanged between the process streams ($Q_{i,r} > 0$ for hot streams, $Q_{i,r} < 0$ for cold streams, in kW); R is the heat cascaded from the higher ($r + 1$) to the lower (r) intervals of temperature (kW); N_ω is the number of units available in the utility systems; B is the exergy flow rate of the resources and products (kW); q are the cooling or heating flows supplied by the utility systems (kW), and W is the power produced by the utility systems and the chemical processes, or exported to/imported from the grid (kW). The costs of the inputs and outputs of the chemical plants are adopted as $c_{NG} = 0.032$ EUR/kWh; $c_{EE} = 0.07$ EUR/kWh; $c_{Oil} = 0.018$ EUR/kWh; $c_{Chips} = 0.016$ EUR/kWh; $c_{Wood} = 0.013$ EUR/kWh; $c_{NH3} = 0.098$ EUR/kWh; $c_{Pulp} = 0.144$; EUR/kWh; $c_{CO2market} = 0.0084$ EUR/kg [4,47].

The use of a mixed integer linear programming (MILP) optimization method reduces the computational time at the expense of a reduced accuracy of the modelling and simulation approach. However, the preliminary results of a MILP solution are relevant to identify the plant-wide integration opportunities and to filter less interesting or even infeasible solutions for the integration of the heat pumping systems in the industrial processes. This approach spotlights potential conflicts and synergistic interactions between the heat pumping systems and the existing heating technologies, so that the best arrangement with the minimum number of modifications can be recommended. In any case, more detailed engineering designs are necessary to effectively integrate the proposed energy systems, based on the project-specific constraints. Assumptions related to the nature of the electricity mix and the upstream supply chains may also modify the results obtained in this analysis, thus, the results should be considered in the light of those hypotheses presented.

Performance indicators

The relative exergy efficiency $\left(\eta_{ex} = B_{consumed,\ ideal}/B_{consumed,\ actual}\right)$ is proposed as indicator to quantify the deviation from the minimum theoretical exergy consumption needed to make up the main industrial and chemical products (i.e. $B_{consumed,\ ideal} = B_{ammonia}\ \ or\ B_{pulp}$), in contrast to the actual exergy of the resources consumed ($B_{consumed,\ actual}{=}B_{natural\ gas} + B_{oil} + B_{wood} + B_{chips} \pm W_{Elec\ Grid}$).

The total CO_2 emissions, encompassing both direct and indirect CO_2 emissions, are calculated according to Eq.(4):

$$CO_{2,Spec}\left[\frac{t_{CO_2}}{t_{\mathrm{Product}}}\right] = \left[\frac{f_{Elec\ Grid} \times W_{Elec\ Grid} \times r_{CO_2 Elec\ Grid}}{1000} + \sum_{Wood,\ Chips\ Natural\ gas,\ Oil} f_i \frac{B_i}{b_i^{CH}}\left(I_{CO_2,\ i}\cdot 3600 + \frac{r_{CO_2,\ i} \times b_i^{CH}}{1000}\right)\right] \times \frac{1}{m_{\mathrm{Product},\ i}} \tag{4}$$

where r_{CO2} is the indirect emission factor of electricity, oil, natural gas and biomass imported (g_{CO2}/kWh); b^{CH} is the specific chemical exergy of the energy inputs; and I_{CO2} is the mass carbon content thereof ($kgCO_2/kg_{fuel}$), reported in [48]. Lastly, total revenue is calculated by discounting the additional investment cost of the heat pumping technology, Eq.(5):

where Z is the investment cost (EUR) and $Annfac$ is the annualization factor, which considers an interest rate of 6 % (assumed for incentivized decarbonization technologies) and the fact that modern HPs currently may last around 20 years with proper maintenance and operation [49]. The costs of the heat pump and the mechanical vapor recompression are assumed as 450–700 EUR/kW for heating capacities below 500 kW, and 250–400 EUR/kW for mechanical vapor recompression units (>10 MW) [5,35].

Results and discussion

The performance of the two conventional layouts of an ammonia plant and a pulp mill, is compared to that of the scenarios in which a heat pumping system is installed in those industrial plants. The minimum energy requirement is reported and the energy consumption remarks are discussed. The integrated composite curves of the baseline and revamped cases are described and used to correctly integrate the utility systems, with emphasis on the heat pump setups. Finally, the thermodynamic, environmental and economic indicators are used to (i) map and rank the suitability of the competing configurations, (ii) spotlight the avoidable sources of inefficiency, and (iii) clarify the effect of the carbon taxation and the ratio between the costs of the energy inputs.

Exergy consumption remarks and energy integration performance

Table 1 shows the exergy consumption of the conventional and revamped layouts of the ammonia plant and the pulp mill when no carbon taxation is applied. Accordingly, the conventional ammonia plant consumes two times more natural gas as utility fuel than the solution integrating a heat pumping system. In the revamped setup, the natural gas is still needed as fuel to supply the heating requirements of the steam methane reformer, as well as to raise steam in the Rankine cycle for combined heat and power supply. In the conventional ammonia plant, only a small amount of electricity is imported and a large amount of waste heat from the utility system is available. This fact renders the activation of a heat pump system unattractive under the conventional scenario. However, when a heat pump unit is integrated, there is a chance to import more electricity and avoid excessive power generation in a relatively inefficient Rankine cycle. As a result, a radical reduction of natural gas used as fuel for steam generation is observed in the ammonia plant. In this way, the correct integration of a heat pump leads to an optimal waste heat recovery below the pinch point, as it is upgraded to provide the heating demands above the pinch temperature. This result can be illustrated by the integrated curves of an ammonia plant without (Fig. 3a) and with a heat pump system (Fig. 3b), respectively. The sharp reduction of cooling water use and steam generation leads to the minimization of the area enclosed between the utilities (*blue*) and the process (*red*) curves, which is in turn an indicator of the exergy destroyed in the heat exchanger network when the Carnot factor ($1\text{-}T_o/T$) replaces the corrected temperature T in the Y axis.

It is worthy to notice that, even with a large electricity import into the ammonia plant, the valorization of the waste heat throughout the chemical units still allows for a self-power generation in the Rankine cycle equivalent to the amount consumed by the heat pump and the refrigeration systems together. For this reason, the optimized solution using a heat pump has an overall exergy efficiency 8 % higher compared

$$Revenue\left[\frac{EUR}{t_{Product}}\right] = \sum_{Ammonia,\ Pulp}\left[f_{Product,i}(B\cdot c)_{Product,i}\right] - \sum_{Naturalgas,\ Oil,\ Chips,\ Wood}\left[f_{Input,i}(B\cdot c)_{Input}\right] + f_{CO_2\ Marketed}(m\cdot c)_{CO_2\ Marketed} - f_{CO_2\ Taxed}(m\cdot c)_{CO_2\ Taxed} \pm f_{Elec\ Grid,Exp/Imp}(W\cdot c)_{Elec\ Grid,Exp/Imp} - \frac{Z_{HP\ or\ MVR} \times Annfac}{8760} \tag{5}$$

Table 1
Exergy consumption remarks of the ammonia plant and the kraft pulp mill with and without heat pump systems.

	Ammonia plant		Pulp mill	
Process layout	**Conventional**	**Heat pump-based**	**Conventional**	**Mechanical vapor recompression-based**
Grid electricity import (GJ/$t_{product}$)	0.65	1.75	0	0
Grid electricity export (GJ/$t_{product}$)	0	0	1.51	1.48
Fuel input type	Natural gas	Natural gas	Wood/Oil	Wood/Oil
Fuel energy import (GJ/$t_{product}$)	6.39	3.07	0 (chips)/0.98 (oil)	1.81(chips)/0.98 (oil)
Feedstock input	Natural gas	Natural gas	Wood	Wood
Feedstock consumption (GJ/$t_{product}$)	21.69	21.69	41.15	41.15
Overall exergy consumption (GJ/$t_{product}$)	28.73	26.51	42.13	43.94
Exergy efficiency η_{ex} (%)	64.75	70.15	45.91	43.94
Rankine cycle power generation (GJ/$t_{product}$)	1.47 (Backpressure)	0.70 (Backpressure)	4.42 (Extraction-Condensing)	5.48 (Extraction-Condensing)
Process power demand (GJ/$t_{product}$)	1.56	1.56	2.84	2.84
Cooling tower power demand (GJ/$t_{product}$)	0.17	0.13	0.07	0.11
Heat pump/MVR power demand (GJ/$t_{product}$)	0	0.39	0	0.99
Refrigeration power demand	0.35	0.35	0	0
Cooling requirement (GJ/$t_{product}$)	7.44	7.44	2.24	15.16
Heating requirement (GJ/$t_{product}$)	4.33	4.33	12.23	25.37
Ammonia production (t/day)	1,000	1,000	0	0
Pulp production (t/day)	0	0	880 (air dried)	880 (air dried)

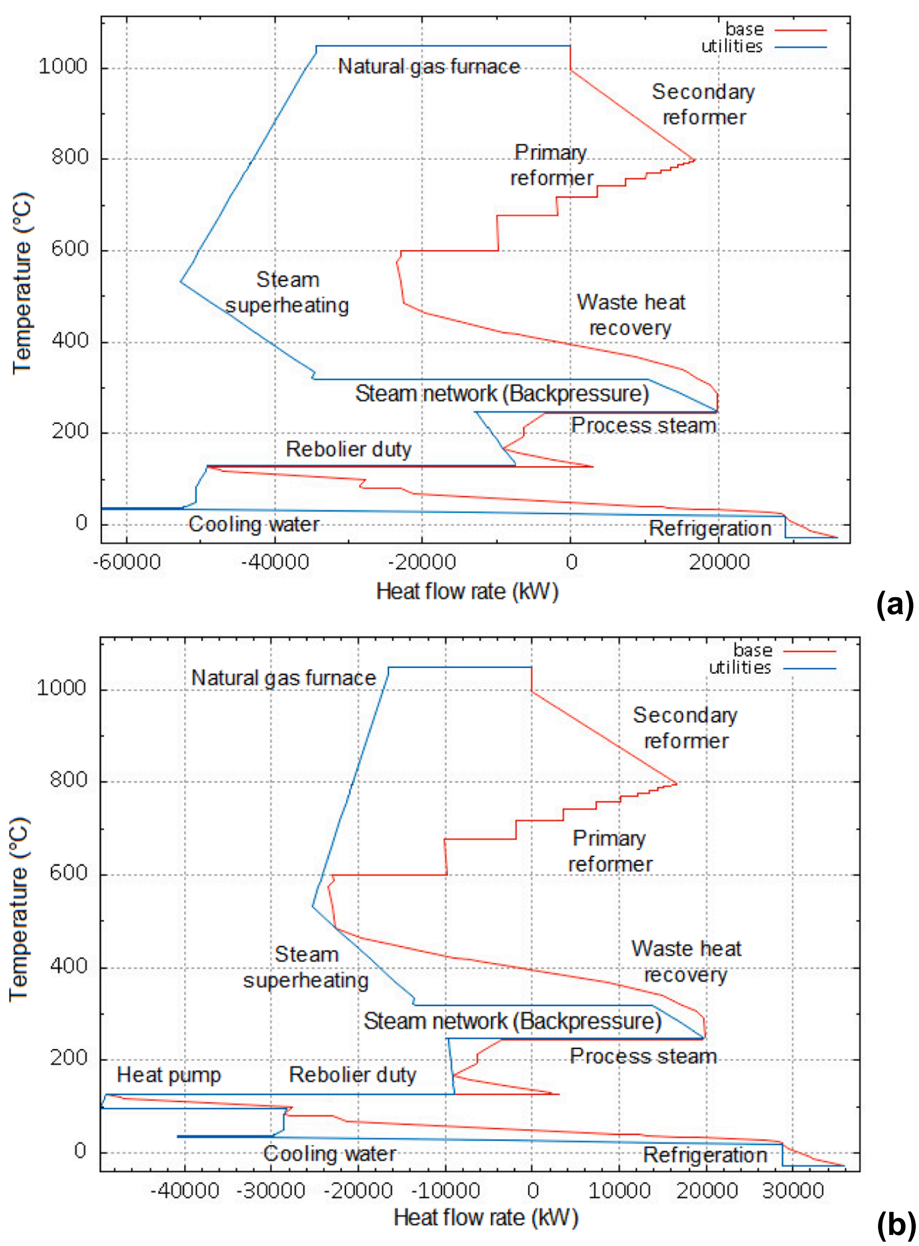

Fig. 3. Integrated composite curves of the ammonia production plant (a) without heat pump and (b) with heat pump integration.

to the typical configuration of the ammonia plant. Fig. 3b also provides important information about the best positioning of the heat pump system. Evidently, the integration of a heat pump system reduces the cooling water demand by 25 % (Fig. 3b), since it removes waste heat at 90 °C from the condenser effluent of the desorption column to upgrade it up to 120 °C to supply the reboiler duty. The positioning of the heat pump below this pinch temperature would lead to an avoidable exergy destruction through electricity wastage, since the electrical energy consumed would be irremediably degraded into heat and rejected to the environment, entailing an increased consumption of the cooling utility.

In addition, if a high temperature heat pump were installed above the identified pinch point, the performance of the electricity conversion would be equivalent to that of an electrical heater (COP = 1), which is clearly not the best energy supply solution, given the excess heat already recovered using a comprehensive steam network. This circumstance calls for a detailed analysis such as that made possible by the study of the integrated composite curves of Fig. 3a-b. Other observation independent from the ammonia plant layout is the waste heat still available at 30–40 °C from the cooling water system. Some studies advocated for the capitalization of this waste heat (~10 MW for the studied cases) to provide waste heat to a district heating network located nearby the industrial fertilizers production complex [50].

Table 1 also compares the exergy consumption of a conventional pulp mill with that of a setup that integrates a mechanical vapor recompression (MVR) in lieu of a multiple effect evaporator (MEE). Fig. 4a-b illustrate the radical modifications in the integrated composite curve when either a MEE or a MVR system is installed. Unlike the ammonia plant, the pulp mill barely benefits from the integration of a MVR system, due to the burning of bark and the imperative recovery process of the strong black liquor. In fact, a huge excess of waste heat available in kraft pulp mills eventually favors the low pressure steam extraction over the surplus power generation (to drive the MVR unit) to provide the exergy required by the drying process. It evidences a sensible relationship between the amount of power consumed in the MVR system and the heat exergy of the low pressure steam fed to the MEE, given by $Q_{drying} \times \Theta \times N_{effects} \sim W_{MVR}$; where Q_{drying} is the heat flow

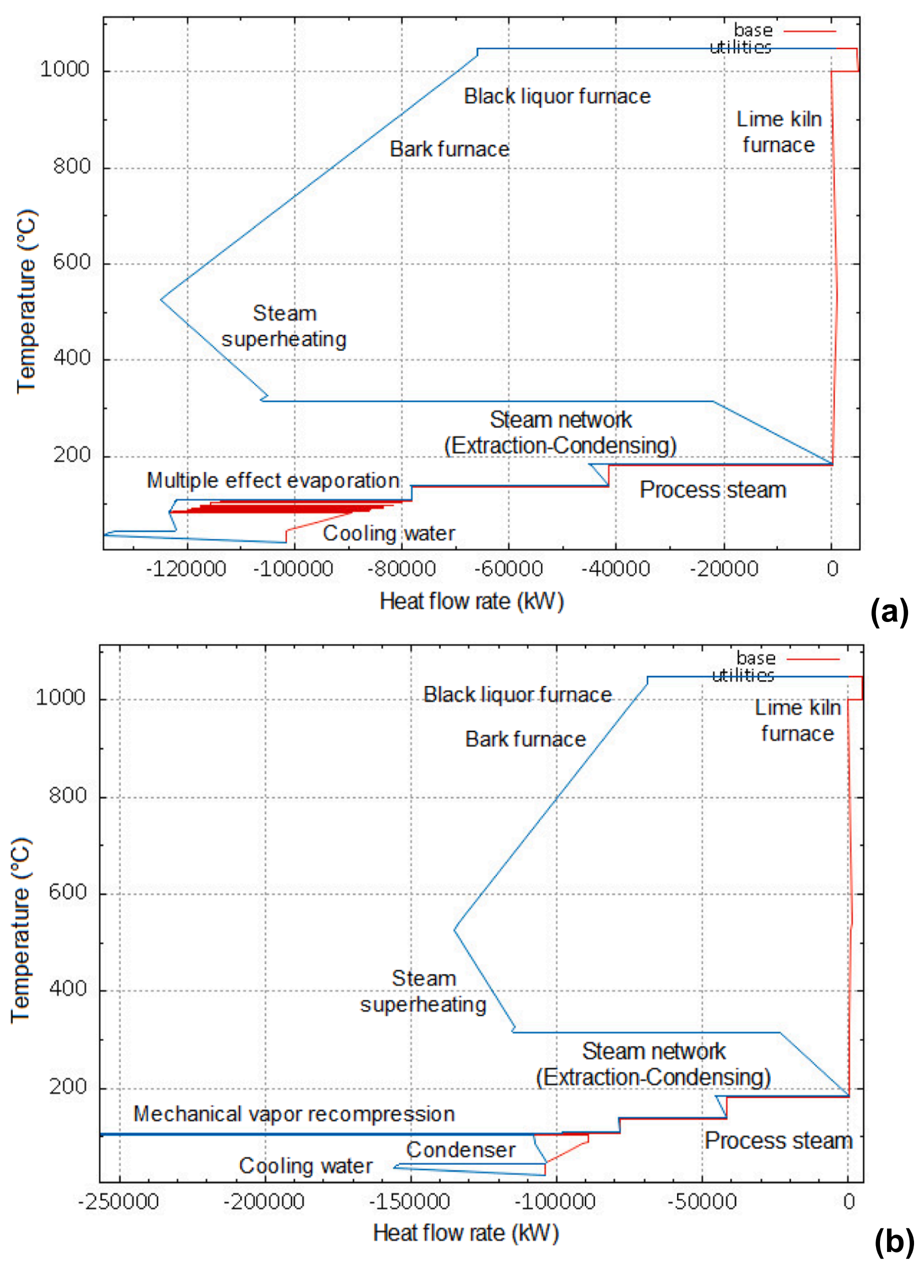

Fig. 4. Integrated composite curves of the pulp mill (a) without mechanical vapor recompression and (b) with mechanical vapor recompression.

rate provided by the steam network to the first effect of the MEE; Θ is Carnot factor ($1-T_o/T_{steam}$), and $N_{effects}$ is the number of effects in the MEE. W_{MVR} stands for the power consumed by the MVR system. On the one hand, as $N_{effects}$ increases (in practice, affordable number of effects is limited to 4–6), the thermodynamic advantage shifts in favor of the MEE system ($Q_{drying} \times \Theta \times N_{effects} < W_{MVR}$). On the other hand, as $N_{effects}$ reduces, the integration of a MVR unit becomes more and more attractive, as the heat exergy of the steam used in the first evaporator becomes larger than the mechanical exergy required for concentrating the black liquor in a falling film evaporator heated by a MVR unit (i.e. $Q_{drying} \times \Theta > W_{MVR}$).

For a specific pulp mill with 5 MEEs, the integration of a MVR becomes slightly less efficient (2 percentage points) than the conventional setup. This fact can be explained by an additional consumption of chips as fuel in the MVR-based scenario (4 %) to maintain the level of power exported and supply the power required by the pulp mill. The cooling water consumption also increases in the MVR-based scenario (20 %) due to the higher power generation in the Rankine cycle as shown in Table 1 and Fig. 4a-b. In summary, due to the inherently large waste heat availability at the pulp mill, the attractiveness of the integration of a MVR is strongly dependent on the number of MEEs, despite the high COP (>10) of the heat pumping technology. Anyhow, the performance of both setups does not differ significantly in terms of exergy efficiency, thus the alternative kraft pulp mill with a MVR system still appears to be competitive vis-à-vis a conventional layout. Mechanical vapor recompression units have other advantages, e.g. faster and reliable steam superheating using electricity imported or generated inside the mill. The combination of MVR and MEE [51], or even MVR, MEE and crystallization evaporation [52], has been proposed to enhance the component-wise economic performance and increase the energy efficiency of black liquor drying process. Despite the fact that substantial savings in operating costs (77 %) for the MVR-assisted MEE black liquor evaporation system have been reported, those analyses did not consider the impact of the overall energy balance and the suitability of a heat pumping system in the plant-wide scope. Thus, it is important to stress that the black liquor concentration system of a chemical pulp is part of an integrated energy system and the misplacement of any heating technologies around it may have unexpected consequences on the total energy consumption and export of the industrial site.

Economic and environmental performance

Table 2 summarizes costs and revenues of the ammonia plant and the kraft pulp mill equipped with and without a heat pump, whereas Table 3 shows the respective emissions balance. Lower operating costs of the ammonia plant with a heat pump (HP) allows for higher revenues (2 %), despite the additional capital cost associated (2.55 EUR/t_{NH3}). In fact, the increase in efficiency (8 %) due to installation of a HP unit in the syngas purification section of an ammonia plant seemingly favors a drop in the amount of natural gas consumed as fuel, even for a cost ratio of $c_{EE}/c_{NG} \sim 2$. This result exemplifies how an increment in efficiency can cause a drop in total costs, even at the expense of an incremental investment cost, which is one of the major issues regarding the integration of the heat pump technology [7]. Moreover, due to an effective waste heat recovery and electrification strategy, the reduced consumption of natural gas in an ammonia plant equipped with a HTHP also translates into 36.5 % less CO_2 emissions. The installation of a HTHP into an ammonia production plant may also benefit from more stringent scenarios of carbon taxation, even for conditions of more volatile energy markets, as it will be discussed later in the sensitivity analysis section.

On the other hand, due to higher chips consumption and more expensive heat pumping unit per ton of product (5.95 EUR/t_{Pulp}), a MVR integrated to a pulp mill is seemingly less economically attractive (-3%) than a conventional pulp mill. Actually, based on Tables 1-3, a drop in exergy efficiency in a pulp mill equipped with a MVR unit (-4%) entails 3 % lower total revenues, and about 1 % increase in the net fossil CO_2 emissions. The negligible variation of the net fossil CO_2 emissions for the pulp mill is due to the fact that the direct biogenic emissions are assumed as circular emissions, and the indirect fossil emissions come from the biomass and electricity supply chains. Moreover, the only contribution to the direct fossil CO_2 emissions in the pulp mill comes from the oil consumption in the lime kiln. Notwithstanding, it is remarkable that the fossil indirect emissions of the pulp mills can be up to threefold the direct emissions from the fuel oil combustion. In fact, the supply chains of the pulp mills have been regarded as important contributors to the environmental impact of the integrated biorefineries [53]. More interestingly, the net fossil emissions in the pulp mills are comparable to the direct emissions in the natural gas-based ammonia plants, which is explained by higher biomass consumption to operate the pulp mills and the lower conversion efficiency of their cogeneration systems.

As a conclusion, although standalone MVR systems could be regarded as potential technologies for upgrading the waste heat available in the pulp sector [9], the overall energy balance of the industrial plant should be firstly analyzed in detail in order to identify possible conflicts among existing and revamping energy technologies. In fact, the efficiency advantage of a MVR unit increases with the pressure and the temperature of the saturated steam produced [9]. Thus, if waste heat recovered in the form of steam is already available at high pressure and temperature due to the inherent chemical recovery processes in the pulp mill, the integration of a MVR turns out to be just as good as a complementary solution and its comparative performance rather relies on the conditions adopted for its MEE counterpart. In other words, if a MEE unit exhibits higher thermal energy consumption owed to imperfect isolation, suboptimal number of evaporators or pressure levels design, the installation of MVR or MVR-aided MEE could be still a good solution for revamping a pulp mill [51]. In the largest MVR evaporation plant at the Sappi Saiccor pulp mill in South Africa, the process steam is superheated in an newly installed MVR system, which proved to be effective for tackling the steam losses and easing the plant maintenance [35]. However, substantial reductions in the overall energy consumption are not reported as a major achievement. Alternatively, black liquor integrated gasification combined cycles that profit from the thermodynamic potential at higher temperatures may increase the electricity generation, which in turn reduces the waste heat available at high temperature, thus enabling favorable conditions to install a MVR in a pulp mill. Other studies used black liquor for producing syngas in integrated pulp mills and ammonia plants, which represents an operative advantage, as the waste heat of the value-added chemicals production plants can be upgraded via a MVR or recovered by a comprehensive steam network at high temperature [47,53].

Sensitivity analysis on the costs of the energy inputs and the CO_2 tax

In the previous analyses, it was considered that the costs of the energy inputs were constant and the CO_2 emissions were not taxed. That approach may offer an incomplete outlook on the suitability of integrating the high temperature heat pump systems into the industrial processes. For this reason, in this section, the effect of introducing a carbon tax similar to that adopted in high income economies, like Switzerland (120 EUR/t_{CO2}) [32], has been studied for the case study of the ammonia production. The reason for not performing the same sensitivity analysis for the pulp mill is that the optimal solutions for that industrial application proved to be relatively insensitive to variations of the energy input costs and the carbon tax in comparison to those of the ammonia plant.

Fig. 5 (A)-(D) show the resulting integrated curves when the costs of the energy inputs are varied for the ammonia plant. The cost of natural gas (c_{NG}) is varied between 0.01 and 0.15 EUR/kWh, whereas the electricity cost (c_{EE}) ranges from 0.01 to 0.5 EUR/kWh. Tables 4a and 5a associate the classification letters in Fig. 5(A)-(D) to each c_{EE}/c_{NG} ratio for a carbon taxation of 0 or 120 EUR/t_{CO2}, respectively. To read those tables, the natural gas and electricity prices are first selected and then

Table 2
Operating incomes, costs and total revenues of the ammonia plant and the kraft pulp mill with and without heat pump systems (carbon tax not included yet).

	Ammonia plant		Pulp mill	
Process layout	**Conventional**	**Heat pump-based**	**Conventional**	**Mechanical vapor recompression-based**
Heat pump CAPEX incl. installation (EUR/$t_{product}$)	0	2.55	0	5.95
Operating incomes (EUR/$t_{product}$)	518.26	518.26	736.67	736.14
Operating costs (EUR/$t_{product}$)	262.17	254.15	153.49	161.53
Total revenue (EUR/$t_{product}$)	256.09	261.57	583.19	568.65

Table 3
Emissions balance of the ammonia plant and the kraft pulp mill with and without heat pump systems.

	Ammonia plant		Pulp mill	
Process layout	**Conventional**	**Heat pump-based**	**Conventional**	**Mechanical vapor recompression-based**
Fossil CO_2 avoided ($t_{CO2}/t_{product}$)[1]	1.42	1.42	0	0
Fossil CO_2 direct emitted ($t_{CO2}/t_{product}$)[2]	0.37	0.18	0.07	0.07
Fossil CO_2 indirect emitted ($t_{CO2}/t_{product}$)[3]	0.15	0.15	0.18	0.19
Net fossil CO_2 emitted ($t_{CO2}/t_{product}$)[4]	0.52	0.33	0.25	0.26

1. Captured in the syngas purification unit; 2. In the pulp mill, due to the consumption of oil in the lime kiln; 3. Considering the extended emissions of the supply chain of commodities; 4. Overall balance considering indirect and direct emissions.

the letter corresponding to the composite curve in the Fig. 5(A)-(D) must be identified. The red point in Table 4a represents the scenario of fixed commodity prices assumed in the previous sections (c_{NG} = 0.032 EUR/kWh; c_{EE} = 0.07 EUR/kWh), for which the carbon tax was considered as 0 EUR/t_{CO2}. Thus, depending on the operational mode imposed, the heat pump can be activated or deactivated: (i) cogeneration Fig. 5(B, C), the HP is deactivated; (ii) cogeneration with intensive electricity import Fig. 5(A,D), the HP is activated.

According to Fig. 5(A)-(D) and Table 4a, the integration of a heat pump strongly depends on the c_{EE}/c_{NG} ratio, even for no carbon tax adopted. The solutions represented by the integrated curves 5(A) and (D) are more likely to occur when c_{EE}/c_{NG} ratio is lower than 2.3. However, as the carbon tax is increased by 120 EUR/t_{CO2}, the new c_{EE}/c_{NG} ratio at which the heat pump integration is preferred can be as high as 5 (see Table 5a). In this regard, the implementation of a carbon tax may be beneficial for the deployment of the heat pump technology in the ammonia plants, especially in scenarios of higher electricity prices, commonly associated to the intermittent electricity generation using renewable sources. The red spot in Tables 4a and 5a indicates that it suffices an increase in the carbon tax from 0 to 120 EUR/t_{CO2} for a heat pump system to become the most suitable option to supply the reboiler duty in the syngas purification unit of the ammonia plant, in lieu of extracting steam in an extraction-condensing steam turbine of the cogeneration system.

It is also observed that for electricity costs from twice to three times larger than the natural gas costs, the ammonia plant configurations obtained are represented by the integrated curves in Fig. 5(B) and (C). These two setups differ from each other by the lower cooling water requirement in the configuration (C), due to a reduced extent of self-cogeneration in the ammonia plant. A careful examination of the integrated curve shown in Fig. 5(C) also reveals that the excess waste heat available from the cogeneration system is reduced and the hot stream associated to the natural gas furnace "retracts", in comparison to the integrated curve shown in Fig. 5(B). Thus, even a partial import of electricity triggers a shift from a fully cogeneration mode (based on fossil resources) to an operating regime in which the activation of a high temperature heat pump unit is imminent. Further reduction of the c_{EE}/c_{NG} ratio promotes the selection of operating regimes that favor the installation of heat pump units at the expense of an intensive electricity import, Fig. 5(A) and (D). This is a remarkable difference between the integration potential of a high temperature heat pump in an ammonia production plant and a MVR unit in a pulp mill, as the latter inherently presents a larger excess of high-grade waste heat. Also, in the ammonia plant, the characteristic Grand composite curve is strongly affected by the energy demand profile of the chemical absorption system for syngas purification. In effect, a plateau-like evaporation profile that extends to the left in Fig. 5 imposes a process pinch point at around 120 °C, which demands a careful integration strategy to avoid the needless installation of a costly HP system, especially in cases like Fig. 5 (B) and (C). The energy consumption in the syngas purification unit and the pinch point temperature of the ammonia plant have been also found to be affected by the type of carbon capture unit adopted (i.e. chemical or physical absorption-based) [4], rendering the integration strategy of a HP system unnecessary or even impracticable in certain cases.

Table 6 shows the sensitivity maps of the efficiency of the ammonia plant with and without heat pump system for different c_{EE}/c_{NG} ratios, considering carbon taxation of 0 and 120 EUR/t_{CO2}. Table 6a shows that an increase in more than 8 percentage points is attainable when the cost of the electricity is low enough (<0.05 EUR/kWh) to enable the heat pump technology integration. The intensive import of renewable electricity produced at higher efficiency (e.g. by a hydropower-based electricity mix) has a positive impact on the overall exergy efficiency of an ammonia plant equipped with a heat pump technology [54]. As expected, the lowest exergy efficiency corresponds to the case in which natural gas is consumed to generate combined power and steam in the steam network of the ammonia plant. Oversized steam networks have been historically pointed as one of the main sources of the inefficiencies of the old ammonia plants [22,23]. Thus, a synergistic combination of heat pump and less energy-intensive carbon capture solvents can help to optimally size the cogeneration unit and avoid condensation losses [4]. Meanwhile, according to Table 6b, the introduction of a carbon tax (120 EUR/t_{CO2}) may promote the partial substitution of the conventional utility systems based on fossil resources, while increasing the energy conversion efficiency by 9 percentage points, even for much higher c_{EE}/c_{NG} ratios.

It is also interesting to compare the environmental performance of the ammonia plant layouts with and without a heat pump system. As it can be seen from Table 7a-b, the CO_2 emissions can be almost halved if an ammonia plant shifts its operation strategy from a standalone cogeneration mode (Fig. 5B) towards a mixed mode with electrification using heat pump systems (Fig. 5D). This result has been shown in Table 3 for a scenario without any carbon taxation and with a fixed c_{EE}/c_{NG} ratio. However, the relative advantage becomes more evident in scenarios of stringent carbon taxations (see Table 7b). For instance, even for the same ratio of c_{EE}/c_{NG} = 0.25/0.08, the introduction of a carbon tax may favor the heat pump installation, which reduces the environmental impact from 0.64 t_{CO2}/t_{NH3} to 0.34 t_{CO2}/t_{NH3}. In this regard, the internalization of the CO_2 emissions impact of the bulk chemical sectors, such

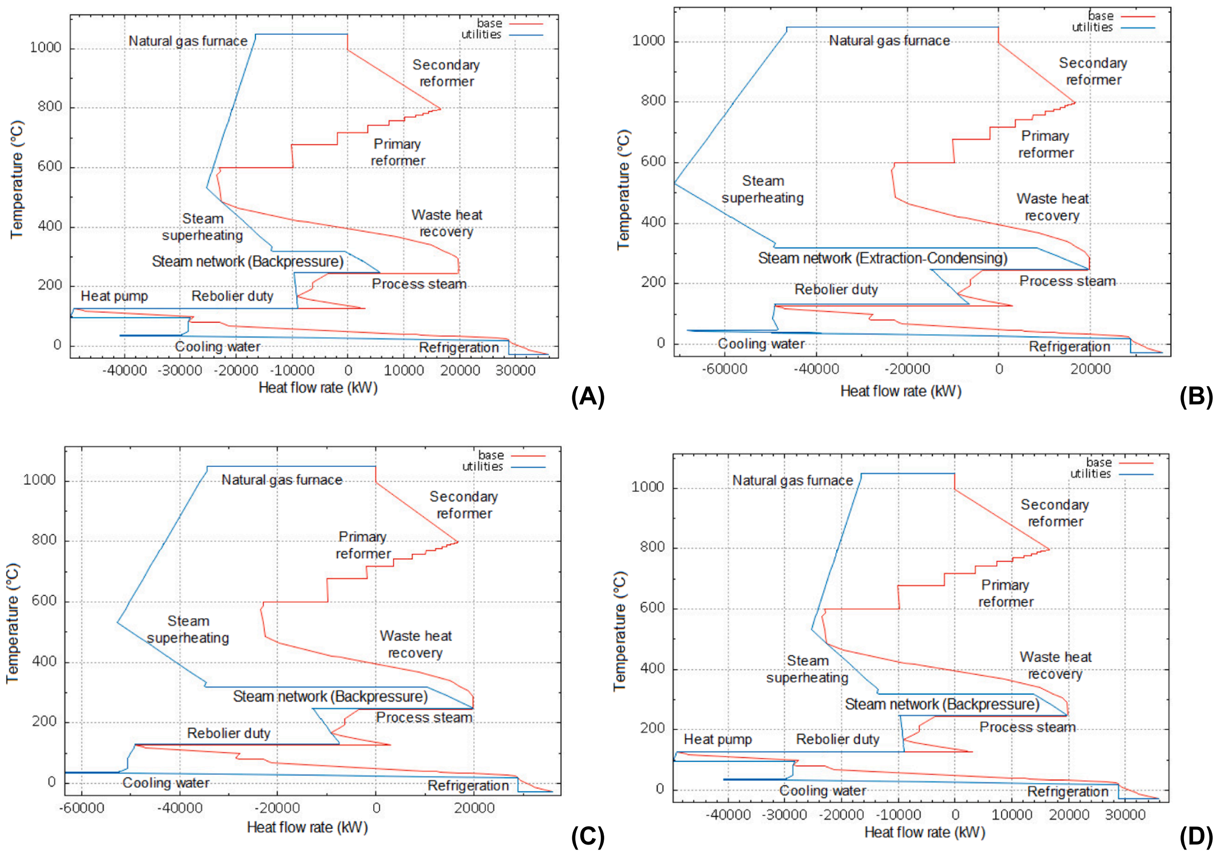

Fig. 5. Integrated curves of the ammonia plant for different scenarios of carbon taxation and c_{EE}/c_{NG} ratios. See Tables 4a-b and 5a-b for information about the classification letters.

Table 4
Sensitivity maps for the decision support on the integration of a heat pump to an ammonia plant considering a carbon taxation of 0 EUR/t_{CO2} and different c_{EE}/c_{NG} ratios (*c* in EUR/kWh): (a) classification map of the integrated curves shown in Fig. 5A-D; (b) status of the HP integration, No:0 or Yes:1.

		cEE										
		0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
	0.01	A	B	B	B	B	B	B	B	B	B	B
	0.02	A	C	B	B	B	B	B	B	B	B	B
	0.03	A	D	[illegible]	B	B	B	B	B	B	B	B
	0.04	A	D	C	B	B	B	B	B	B	B	B
	0.05	A	A	D	C	B	B	B	B	B	B	B
cGN	0.06	A	A	D	C	B	B	B	B	B	B	B
	0.07	A	A	D	D	C	B	B	B	B	B	B
	0.08	A	A	D	D	C	B	B	B	B	B	B
	0.09	A	A	A	D	D	C	B	B	B	B	B
	0.1	A	A	A	D	D	C	C	B	B	B	B
	0.15	A	A	A	A	D	D	D	D	C	C	B

(a)

		cEE										
		0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
	0.01	1	0	0	0	0	0	0	0	0	0	0
	0.02	1	0	0	0	0	0	0	0	0	0	0
	0.03	1	1	0	0	0	0	0	0	0	0	0
	0.04	1	1	0	0	0	0	0	0	0	0	0
	0.05	1	1	1	0	0	0	0	0	0	0	0
cGN	0.06	1	1	1	0	0	0	0	0	0	0	0
	0.07	1	1	1	1	0	0	0	0	0	0	0
	0.08	1	1	1	1	0	0	0	0	0	0	0
	0.09	1	1	1	1	1	0	0	0	0	0	0
	0.1	1	1	1	1	1	0	0	0	0	0	0
	0.15	1	1	1	1	1	1	1	1	0	0	0

(b)

Table 5
Sensitivity maps for the decision support on the integration of a heat pump to an ammonia plant considering a carbon taxation of 120 EUR/t_{CO2} and different c_{EE}/c_{NG} ratios (*c* in EUR/kWh): (a) classification map of the integrated curves shown in Fig. 5A-D; (b) status of the HP integration, No:0 or Yes:1.

(a)

cGN \ cEE	0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.01	A	D	C	B	B	B	B	B	B	B	B
0.02	A	A	D	B	B	B	B	B	B	B	B
0.03	A	A	[illegible]	C	B	B	B	B	B	B	B
0.04	A	A	D	D	B	B	B	B	B	B	B
0.05	A	A	D	D	C	B	B	B	B	B	B
0.06	A	A	A	D	D	C	B	B	B	B	B
0.07	A	A	A	D	D	C	B	B	B	B	B
0.08	A	A	A	D	D	D	B	B	B	B	B
0.09	A	A	A	D	D	D	C	C	B	B	B
0.1	A	A	A	D	D	D	D	C	B	B	B
0.15	A	A	A	A	A	D	D	D	D	C	C

(b)

cGN \ cEE	0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.01	1	1	0	0	0	0	0	0	0	0	0
0.02	1	1	1	0	0	0	0	0	0	0	0
0.03	1	1	1	0	0	0	0	0	0	0	0
0.04	1	1	1	1	0	0	0	0	0	0	0
0.05	1	1	1	1	0	0	0	0	0	0	0
0.06	1	1	1	1	1	0	0	0	0	0	0
0.07	1	1	1	1	1	0	0	0	0	0	0
0.08	1	1	1	1	1	1	0	0	0	0	0
0.09	1	1	1	1	1	1	0	0	0	0	0
0.1	1	1	1	1	1	1	1	0	0	0	0
0.15	1	1	1	1	1	1	1	1	1	0	0

Table 6
Sensitivity maps of the efficiency of the ammonia plant with and without heat pump system for different c_{EE}/c_{NG} ratios (*c* in EUR/kWh), considering carbon taxation of (a) 0 and (b) 120 EUR/t_{CO2}.

For tax 0

(a)

cGN \ cEE	0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.01	70%	61%	61%	61%	61%	61%	61%	61%	61%	61%	61%
0.02	70%	65%	61%	61%	61%	61%	61%	61%	61%	61%	61%
0.03	70%	69%	62%	61%	61%	61%	61%	61%	61%	61%	61%
0.04	70%	69%	65%	62%	61%	61%	61%	61%	61%	61%	61%
0.05	70%	70%	69%	65%	61%	61%	61%	61%	61%	61%	61%
0.06	70%	70%	69%	65%	62%	61%	61%	61%	61%	61%	61%
0.07	70%	70%	69%	69%	65%	62%	61%	61%	61%	61%	61%
0.08	70%	70%	69%	69%	65%	62%	62%	61%	61%	61%	61%
0.09	70%	70%	70%	69%	69%	65%	62%	61%	61%	61%	61%
0.1	70%	70%	70%	69%	69%	65%	65%	62%	61%	61%	61%
0.15	70%	70%	70%	70%	69%	69%	69%	69%	65%	65%	62%

For tax 120

(b)

cGN \ cEE	0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.01	70%	69%	65%	61%	61%	61%	61%	61%	61%	61%	61%
0.02	70%	70%	69%	62%	61%	61%	61%	61%	61%	61%	61%
0.03	70%	70%	69%	65%	62%	61%	61%	61%	61%	61%	61%
0.04	70%	70%	69%	69%	62%	62%	61%	61%	61%	61%	61%
0.05	70%	70%	69%	69%	65%	62%	61%	61%	61%	61%	61%
0.06	70%	70%	70%	69%	69%	65%	62%	61%	61%	61%	61%
0.07	70%	70%	70%	69%	69%	65%	62%	62%	61%	61%	61%
0.08	70%	70%	70%	69%	69%	69%	65%	62%	62%	61%	61%
0.09	70%	70%	70%	69%	69%	69%	65%	65%	62%	61%	61%
0.1	70%	70%	70%	70%	69%	69%	69%	65%	62%	62%	61%
0.15	70%	70%	70%	70%	70%	69%	69%	69%	69%	65%	65%

as the nitrogen fertilizers, proves to be a critical condition for encouraging economic activities traditionally based on fossil inputs to adopt more efficient and environmentally friendly energy technologies. Clearly, other emissions associated to natural gas leakages should be also considered, which reinforces the goal of reducing transportation and consumption of non-renewable natural gas, while using more electricity to reduce the atmospheric emissions. In any case, the integration of heat pump systems must come along other integration approaches, in which renewable energy resources are fundamental to provide not only the fuel needed for supplying heat, but also the

Table 7
Sensitivity maps of the CO_2 emissions of the ammonia plant with and without heat pump system for different c_{EE}/c_{NG} ratios (*c* in EUR/kWh), considering carbon taxation of (a) 0 and (b) 120 EUR/t_{CO2}.

For tax 0

	cEE										
cGN	0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.01	0.33	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
0.02	0.33	0.52	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
0.03	0.33	0.34	0.64	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
0.04	0.33	0.34	0.52	0.64	0.65	0.65	0.65	0.65	0.65	0.65	0.65
0.05	0.33	0.33	0.34	0.52	0.65	0.65	0.65	0.65	0.65	0.65	0.65
0.06	0.33	0.33	0.34	0.52	0.64	0.65	0.65	0.65	0.65	0.65	0.65
0.07	0.33	0.33	0.34	0.34	0.52	0.64	0.65	0.65	0.65	0.65	0.65
0.08	0.33	0.33	0.34	0.34	0.52	0.64	0.64	0.65	0.65	0.65	0.65
0.09	0.33	0.33	0.33	0.34	0.34	0.52	0.64	0.65	0.65	0.65	0.65
0.1	0.33	0.33	0.33	0.34	0.34	0.52	0.52	0.64	0.65	0.65	0.65
0.15	0.33	0.33	0.33	0.33	0.34	0.34	0.34	0.34	0.52	0.52	0.64

(a)

For tax 120

	cEE										
cGN	0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.01	0.33	0.34	0.52	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
0.02	0.33	0.33	0.34	0.64	0.65	0.65	0.65	0.65	0.65	0.65	0.65
0.03	0.33	0.33	0.34	0.52	0.64	0.65	0.65	0.65	0.65	0.65	0.65
0.04	0.33	0.33	0.34	0.34	0.64	0.64	0.65	0.65	0.65	0.65	0.65
0.05	0.33	0.33	0.34	0.34	0.52	0.64	0.65	0.65	0.65	0.65	0.65
0.06	0.33	0.33	0.33	0.34	0.34	0.52	0.64	0.65	0.65	0.65	0.65
0.07	0.33	0.33	0.33	0.34	0.34	0.52	0.64	0.64	0.65	0.65	0.65
0.08	0.33	0.33	0.33	0.34	0.34	0.34	0.52	0.64	0.64	0.65	0.65
0.09	0.33	0.33	0.33	0.34	0.34	0.34	0.52	0.52	0.64	0.65	0.65
0.1	0.33	0.33	0.33	0.33	0.34	0.34	0.34	0.52	0.64	0.64	0.65
0.15	0.33	0.33	0.33	0.33	0.33	0.34	0.34	0.34	0.34	0.52	0.52

(b)

feedstock and power consumption. In this regard, the marked dependence of the nitrogen fertilizers sector on natural gas has recently drawn the attention to alternative routes of ammonia [55,56], nitric acid and urea production using biomass and renewable electricity [57,58].

Finally, it is worthy to compare how the overall efficiency relates to the economic attractiveness of the energy systems, as thermodynamic and environmental indicators are not enough to assess the potential gains after investments within firms. Table 8a-b show the total operating revenues (EUR/t_{NH3}) of an ammonia plant as a function of the c_{EE}/c_{NG} ratios for two carbon taxes without and with heat pump system integration. It is worth noticing that, a negative value for revenues indicates an economically favorable scenario, as the optimization problem was defined as the minimization of the positive costs (or, equivalently, maximization of the positive revenues). According to Tables 8a-b, since the ammonia plant depends on natural gas as both feedstock and fuel, the implementation of a high carbon tax in scenarios of high natural gas cost ends up with a sharp drop in total revenues (>30 %). Actually, for the simulated conditions, natural gas costs higher than 0.07 EUR/kWh could make the chemical system economically infeasible, regardless of the electricity cost. Accordingly, the installation of a heat pump system is not a guarantee of reduced total costs, as it may be expected from other economic sectors in which natural gas is only consumed for heating purposes. This outcome warns about the strong dependence of the nitrogen fertilizer sector on the non-renewable, volatile energy markets. It also highlights the importance of diversifying the energy inputs, so that the future economic transitions or tighter environmental regulations do not impact negatively the industrial assets designed to operate over decades.

Other sectors not analyzed in this work, including chemical sectors [47], food and beverage industry [59,60], non-ferrous metals mills [61], drop-in fuels [62], synthetic natural gas production plants [63], and district heating systems [64] have also advocated for the integration of heat pumps, mechanical vapor recompression units or even supercritical and transcritical CO_2 heat pump systems, in order to (i) reduce the energy input via enhanced low-grade waste heat recovery and (ii) promote the gradual electrification of the industrial heat supply. However, major market barriers for the deployment of the heat pump technology have been also identified [7,18]: (i) the insufficient knowledge about the integration of the HP systems to the industrial processes; (ii) the lack of available refrigerants in the high temperature range with a low GWP; and (iii) the high price ratio of electricity to fossil fuel. Meanwhile, the potential taxation of the carbon emissions and the uncertainty about the natural gas price may be decisive aspects pushing towards the defossilization of the heating requirements of the industrial applications, as it has been suggested in the present and in others works, using electrification or cheaper biomass resources [25].

Conclusions

In this work, the integration of high temperature heat pump systems (HTHPs) into two industrial applications, namely, an ammonia plant and a kraft pulp mill, has been evaluated based on thermodynamic, environmental and economic indicators. A combined energy integration and exergy analysis proved to be crucial to correctly integrate the HTHPs into the industrial processes in order to reduce the fossil energy input and the environmental impact related to these industrial facilities:

- The energy consumption in the conventional ammonia plant could be cut down (-8.3 %) by increasing the electricity import and integrating a heat pump in order to supply heat to the reboiler of the syngas purification unit. The integration of a heat pump reduces the cooling requirement in the ammonia plant by 25 %. It capitalizes on the waste heat at 90 °C from the condenser of the desorption column to upgrade it to 120 °C to supply the reboiler duty.
- When the cost of electricity is low enough (<0.05 EUR/kWh) as to enable the integration of a HP technology in an ammonia plant, an increase in exergy efficiency (+8 percentage points) is expected. Also, the CO_2 emissions can be almost halved if an ammonia plant is

Table 8
Sensitivity maps of the total revenues of the ammonia plant as a function of the c_{EE}/c_{NG} ratio for two carbon taxes: (a) CO_2 tax = 0 EUR/t_{CO2} and (b) CO_2 tax = 120 EUR/t_{CO2}. Negative values mean economically attractive scenarios, as the objective function minimizes the total operating cost.

For tax 0

		cEE										
		0.01	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
cGN	0.01	-437	-432	-433	-434	-435	-436	-437	-438	-439	-440	-441
	0.02	-369	-351	-349	-350	-351	-352	-353	-354	-355	-356	-357
	0.03	-300	-277	-265	-266	-267	-268	-269	-270	-271	-272	-273
	0.04	-232	-208	-186	-182	-183	-184	-184	-185	-186	-187	-188
	0.05	-164	-140	-111	-99	-98	-99	-100	-101	-102	-103	-104
	0.06	-95	-72	-43	-21	-15	-15	-16	-17	-18	-19	-20
	0.07	-27	-3	26	54	66	69	68	67	66	65	64
	0.08	42	65	95	123	144	152	152	152	151	150	149
	0.09	110	134	163	192	220	231	236	236	235	234	233
	0.10	178	202	232	261	289	309	318	319	319	318	317
	0.15	520	544	574	603	633	661	689	717	726	735	737

(a)

For tax 120

		cEE										
		0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
cGN	0.01	-410	-387	-370	-369	-370	-371	-371	-372	-373	-374	-375
	0.02	-342	-318	-290	-285	-285	-286	-287	-288	-289	-290	-291
	0.03	-274	-250	-221	-205	-201	-202	-203	-204	-205	-206	-207
	0.04	-205	-182	-153	-125	-118	-118	-119	-120	-121	-122	-123
	0.05	-137	-113	-84	-56	-40	-34	-35	-35	-36	-37	-38
	0.06	-68	-45	-15	13	41	47	49	49	48	47	46
	0.07	0	24	53	82	110	125	133	133	132	131	130
	0.08	68	92	122	151	179	207	212	216	216	215	214
	0.09	137	160	190	219	247	275	290	299	300	300	299
	0.10	205	229	258	288	316	344	372	377	383	383	383
	0.15	547	571	600	630	660	688	716	744	772	785	794

(b)

equipped with a HTHP system (46 % less CO_2 emissions or, equivalently, a reduction from 0.64 t_{CO2}/t_{NH3} to 0.34 t_{CO2}/t_{NH3}).

- The adoption of a carbon tax may favor the installation of a HTHP in order to reduce the environmental impact; however, since the ammonia plant depends on natural gas not only as a fuel, but also as feedstock, high carbon taxes in scenarios of high natural gas costs may sharply reduce the total revenues (-30 %). In the case studies, natural gas costs higher than 0.07 EUR/kWh could make the system economically infeasible, regardless of the electricity cost.
- In the ammonia plant, when the c_{EE}/c_{NG} ratio is large (more than ~2.3), the optimized solution based on the total cost favors the use of natural gas and the steam network, at the expense of a lower cogeneration efficiency. However, as the carbon tax is increased by 120 EUR/t_{CO2}, the new c_{EE}/c_{NG} ratio at which a heat pump integration is still preferred can be as high as 5. This effect is less evident in the studied pulp mill scenarios.
- The performance of the kraft pulp mills based on either a multiple effect evaporator (MEE) and a mechanical vapor recompressor (MVR) system does not differ significantly in terms of exergy efficiency. The drop in exergy efficiency in a pulp mill with a MVR unit (-4%) entails only 3 % lower total revenues, and ~1 % increase in net fossil CO_2 emissions. Thus, the alternative setup is still competitive vis-à-vis the conventional layout.
- The integration of a MVR system for drying the black liquor in an integrated pulp mill proved to be an interesting solution, although to a lesser extent if compared to the case of an ammonia plant. In fact, a large amount of waste heat derived from the inherent chemical recovery processes in the pulp mill makes the integration of a heat pumping technology as much attractive as a series of MEE.
- Due to the elevated costs of the heat pumping technology and in view of the risk perception related to the breakthrough technologies; more subventions and taxes may help boosting the scaling up of the heat pump deployment. Although installing a heat pump is not a warranty of higher efficiencies or revenues, it may boost the efficiency in certain applications. This would be is a step forward towards the defossilization of the heat supply to the industrial energy systems traditionally based on fossil resources.

Declaration of Competing Interest

The authors declare the following financial interests which may be considered as potential competing interests: Daniel Florez-Orrego has been funded by the Swiss Federal Office of Energy (SFOE). Meire Ellen Ribeiro Domingos declares that her financial support was provided by Swiss Excellence Government Scholarship Programme.

Data availability

Data will be made available on request.

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