

# Syngas Production with Thermo-Chemically Recuperated Gas Expansion Systems: An Exergy Analysis and Energy Integration Study

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## **Abstract:**

In spite of the large degree of energy integration in the modern syngas production units, the highly endothermic reactions of steam methane reforming and the combined steam and power generation still require a huge amount of energy that is typically supplied by an expensive natural gas-fired furnace at very high temperatures. Since normally only half of the energy supplied by the furnace is used to carry out the reforming reactions, the remaining heat recovery must be performed in a separate convection train (HRCT). Additionally, the high temperature effluent of the secondary reformer is generally cooled down by producing low temperature steam, increasing the process irreversibility and the losses associated to the excessive amount of condensate. Thus, in this paper, the advantages of introducing a chemically recuperated gas turbine (CRGT) concept to simultaneously carry out the endothermic chemical reactions and recover the exergy available from the autothermal reformer effluent are discussed. In this way, higher temperatures and higher conversions can be attained with lower driving forces. The power required by the air compression as well as other ancillary systems (e.g. air separation unit, carbon capture system, boiler feedwater pumps and recompressor) can also be supplied, while the exergy of the exhaust gases from the turbine is used more efficiently than in typical steam generation systems. Thus, more compact and integrated syngas production plants can be envisaged. Moreover, by introducing more advanced cogeneration features such as air enrichment, process gas reheating and incremental levels of pressures in the reaction-driven components, energy savings together with drastically reduced atmospheric CO<sub>2</sub> emissions and irreversibility can be achieved in the frontend syngas production section. As a result, the average specific exergy destruction and exergy fuel consumption of the proposed CRGT-based configurations are, respectively, 12.0% and 2.7% lower, whereas the specific atmospheric CO<sub>2</sub> emissions are cut down up to 25%, when compared to the conventional syngas production process.

## **Keywords:**

Chemical recuperation, Exergy, Syngas, Energy Integration, Gas Expansion

## **1. Introduction**

The global demand for hydrogen faces an increasing trend, primarily driven by hydroprocessing in refineries and in the chemical industry [1], whereas its potential use in automotive applications will also likely push the production capacity even further [2]. Despite the fact that some efforts to produce hydrogen from renewable sources such as solar and biomass energy have been considered [3], the cheapest route remains to be the steam reforming of natural gas. However, conventional

reforming still presents many disadvantages regarding the way in which the waste heat recovery is achieved [4]. The customary practice consists of the use of a natural gas-fired furnace to supply the energy to the catalytic tubes of the primary reformer. Nevertheless, since barely half of the exergy in the combustion gases can be effectively recovered in the reformer, the conventional reforming process requires the installation of an additional convection train (HRCT) for heat recovery purposes [5]. Therein, the waste heat is generally used to raise steam at lower temperatures (< 300 °C) than those found elsewhere in the conversion process, entailing an avoidable irreversibility [6]. As part of the efforts to improve these shortcomings, this paper investigates the integration of a novel application for the *Chemically Recuperated Gas Turbine* (CRGT) concept to a syngas production plant, intended to supply a typical ammonia synthesis loop (H<sub>2</sub>/N<sub>2</sub> 3:1). The convenience of a CRGT system lies in the simultaneous existence of both endothermic and exothermic chemical conversion technologies in the syngas production units, which could be appropriately coupled via gas heated reformers (GHR) and waste heat recovery systems. Hence, the readily available exergy of the autothermal reformer effluent could be better exploited to produce power, replacing the conventional role of the ATR effluent as a source for steam generation.

The conventional CRGT concept has been previously studied by different authors looking for improvements in applications of electricity generation [7-11]. Harvey and Kane [7] performed a second law analysis based on an ABB GT26 gas turbine with reheat and chemical recuperation via methane steam reforming, achieving a methane conversion close to 27%. As expected, an improved performance has been obtained at higher temperatures and lower pressures in the reformer. Moreover, the exergy destroyed in the heat recovery steam generator (HRSG) is reported as threefold that in the reformer, corroborating the fact that the generation of steam implies substantially higher exergy destruction rates due to the lower temperature involved. Finally, the authors concluded that further parametrical and process flowsheet modifications may improve the overall efficiency, e.g. by using dual pressure chemically recuperated gas turbine systems with different pressures and steam-to-carbon ratios that align the optimal operating conditions in each reformer. Bearing that in mind, Carapellucci and Milazzo [8] investigated the differences between one single and two dual pressure configurations with an ABB GT24 gas turbine. The dual pressure configurations differed in the steam-to-carbon ratio supplied to the reformer, one with the same steam-to-carbon ratio (S/C) in both reformers, and the other configuration with separately optimized S/C ratios. As a results, when the S/C ratios aligned with the optimal levels of pressure, the methane conversion, heat recovery and plant efficiency are enhanced at the same time that steam production and power generation are increased. The result is a higher efficiency (53.8%) and a power output comparable to that of a combined cycle, which reinforces the position of the CRGT cycle as a competitive thermoelectric alternative.

Kesser et al. [10] built, upon a basic CRGT cycle (i.e. no reheat), two reference cases with different compression ratios and compared them with a combined cycle (CC), a steam injected gas turbine cycle (STIG) and an open gas turbine system (OCGT). They found that the cycle with chemical recuperation follows closely the performance of the combined cycle, presenting the second highest efficiency, whereas the STIG cycle showed the second highest specific power generation, rendering it a more attractive, simpler and less costly option than an advanced CRGT cycle. Adelman et al. [11] revised various conceptual designs for the steam methane reformer in terms of the performance

and size of the CRGT system. The proposed designs evolved by either adding a preheater, changing the diameter of the catalytic tubes, adding heat transfer intensification methods such as roughness and fins to the tubes, or even utilizing different catalyst reactivity, all motivated by the goal to find near-minimum catalyst volumes. The results pointed towards higher reforming temperatures as a direct way to increase conversion of methane and reduce the complexity and volume of the system. Even though most of the efforts have been devoted to medium-to-large scale power generation systems, decentralized approaches have gained renovated interest. More recently, Nakagaki et al. [9] studied the feasibility of a chemical recuperation system applied to microturbines (30-300 kW). The study revealed the practicality of the integration of CRGT concepts to existing power generation systems, either microturbine or MW-class turbines. A catalyst with 2% Ru content reportedly shows the best performance in terms of reaction rates at temperatures as low as 350 °C, whereas conversions as high as 51% have been claimed.

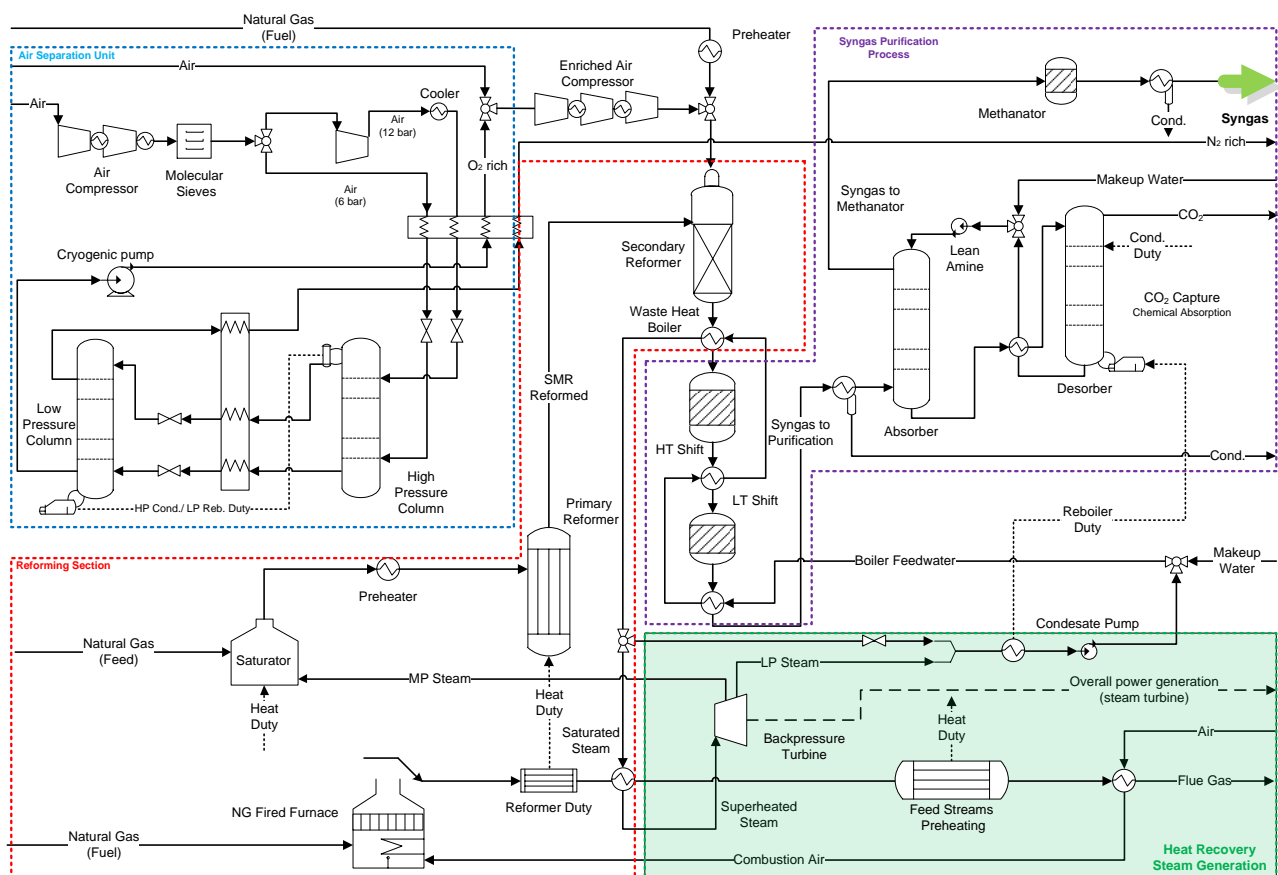
Differently from the research works reviewed hitherto, based on power generation concepts with dedicated combustion chambers, other opportunities for profiting the readily available exergy embodied in the exothermic reactor effluents (e.g. partial oxidation combustors, autothermal reformers, methanol and ammonia converters, etc.) have been thoroughly discussed [12, 13]. Some examples include the implementation of an expansion device that directly produces shaft work from the exergy of the ammonia reactor effluent in lieu of using it for raising steam [14, 15]. Despite the fact that this approach does not actually render the ammonia production unit self-sufficient in terms of power demand, a reduction of the specific power consumed (44-75%) is reported when compared to the use of a heat recovery steam generator. Furthermore, as this approach represents a more efficient way of profiting the thermo-mechanical exergy of the process stream, it also reduces the degradation of the thermodynamic potential of the chemical system [16]. Similarly, Agee et al. [17] described the application of a substoichiometric, simultaneous combustion and reforming process of natural gas in order to produce syngas in a methanol manufacturing plant. By using the autothermal reformer as an enriched air combustor, the highly exothermal reaction supplies the reforming duty in a single pressurized vessel, whereas the expansion of the reactor effluent is able to provide some of the power required for air compression and separation purposes.

In more advanced technologies, such as partial oxidation gas turbines [18], a mixture of methane and steam at high pressure is partially oxidized in a catalytic adiabatic reactor that replaces the conventional combustor chamber of a OCGT. In this way, the low molecular weight fuel gas produced at high temperature, mainly composed of hydrogen and carbon oxides, is expanded to generate mechanical power. Henceforth, the produced gas is completely burned in a bottoming cycle so that the reaction enthalpy released can be supplied to a downstream chemical process. The specific mechanical power produced is reportedly about 6-9% of the LHV of the fuel, which renders the partial combustion gas turbine system also a '*fuel producer*' technology [18]. It must be observed that these approaches substantially differ from that one patented more recently by Keller et al. [19] in which the cogeneration of hydrogen and power is achieved through the integration of two physically separate hydrogen and power generation units. The hydrogen production unit comprises a gas heated reformer, followed by a water gas shift reactor and a hydrogen separation unit. These units produce a purified hydrogen stream and a byproduct consisting of a hydrocarbon-rich fuel stream. The byproduct stream is burned in a conventional combustion chamber of a gas

turbine along with an oxygen-rich stream, and eventually used to provide heat to the gas heated reformer. This approach has been also reported by Alves and Nebra [20, 21] who developed the exergoeconomy analysis of the hydrogen production from natural gas by using an autothermal reformer and a separate gas turbine cogeneration system. Notwithstanding, the suitability of the integration of an autothermal reformer (ATR) to a chemically recuperated gas turbine (CRGT) concept, in order to exploit the exposed advantages of the simultaneous syngas and power production, has not been proposed so far, neither suggested as a part of the *frontend* of an ammonia production plant. Thus, by considering (i) the highly irreversible nature of complete combustion and (ii) the stack losses associate to both the fired furnace of the primary reformer and the combustion chamber of the open gas turbine cycle, along with (iii) the exergy losses associated to the excess steam generation and its subsequent condensation; four novel approaches, based on the CRGT concept, are proposed for the production of syngas intended to be fed to a *backend* industrial ammonia loop. These novel setups are aimed to improve the energy integration capabilities at higher temperatures and reduce the amount of atmospheric emissions, by intensifying the rates of *pre-combustion* carbon capture.

## 2. The integration of the Chemically Recuperated Gas Turbine (CRGT) Concept to the Syngas Production Process

Figures 1-5 compare the five configurations of syngas production plants studied. The conventional system shown in Fig. 1 is based on the most common arrangement for hydrogen production via steam methane reforming (SMR) [22].



*Fig. 1. Conventional configuration. Steam network-based utility system.*

The processes comprises a primary reformer (700-800°C) in series with an autothermal secondary reformer (~1000°C), where a fraction of the reformed gas is burnt with the aid of enriched air (30-40%) to provide the heat required to further convert the methane feed. The air separation unit (ASU) consists of a dual pressure column equipped with a condenser-reboiler heat exchanger, in which the cooling effect is produced by throttling a compressed stream of air that exchanges heat with its separate cryogenic fractions (-190°C). For the sake of an enhanced hydrogen production, two intercooled reactors are used to perform the water gas shift reaction at lower temperatures (200-350°C) [12]. Finally, the carbon oxide components present in the syngas are removed by means of a purification section composed of a chemical absorption and a methanation system. According to Fig. 1, the waste heat released along the chemical process is recovered by using an integrated steam network, so that the additional fuel consumption required to supply both the power and heat demands of the plant can be reduced (reactants preheating, endothermic reactions, etc.) [23]. Consequently, the valuable waste heat exergy recoverable from the secondary reformer effluent is used to produce steam, which in turn needs to be superheated in a separate HRCT. The superheated steam is eventually expanded in a steam turbine, supplying both the power and steam demands.

Meanwhile, the four novel approaches proposed for the syngas production, based on the chemically recuperated gas turbine (CRGT) concept, are illustrated in Figs. 2-5. Differently from the conventional layout (Fig. 1), the novel approaches aim to maximize the use of the readily available exergy of the high temperature, pressurized effluent of the secondary reformer. This is accomplished by chemically recuperating the physical exergy of the expander outlet stream to reform a saturated natural gas mixture, only after partially or totally supplying the power demand of the chemical plant. Due to the characteristics of the chemical recuperation process, compared to either the simple combustion air preheating or the steam injection, a higher amount of exergy can be embodied in the chemical exergy of the reformed mixture, which further increases the efficiency of the waste heat recovery process [7]. Actually, these four novel approaches (Fig. 2-5) have been conceived to exploit the exposed advantages of the CRGT concept, which may also lead to more compact syngas production systems.

According to Fig. 2, since the combustion progresses simultaneously with the endothermic reactions in the secondary reformer, the amount of water produced in the partial combustion process at higher temperatures directly offers an increased concentration of steam in the catalytic section, which, in turn, increases the equilibrium conversion of the reformer as the concentration of the reactants increases. This is threefold advantageous. Firstly, the losses associated to the release and condensation of the flue gases produced in a separate fired furnace can be reduced [5], as the exergy embodied in the moisture of the combustion gases can be maximally exploited at higher temperatures, rather than producing low-grade superheated steam in a heat recovery convection train (HRCT). Furthermore, (ii) as the combustion gases become also process gas, the excessive dilution of the carbon dioxide with dinitrogen is overcome, thus, allowing for an easier capture process at the expense of an additional energy consumption in the syngas purification system. Finally, (iii) the water produced together with the other reaction products allows a higher power throughput per unit of mass of gas to be produced, which enables the utilization of the exhaust gases

of the expander as the heating source of the downstream chemically recuperated, gas heated methane reformer (CRGHR).

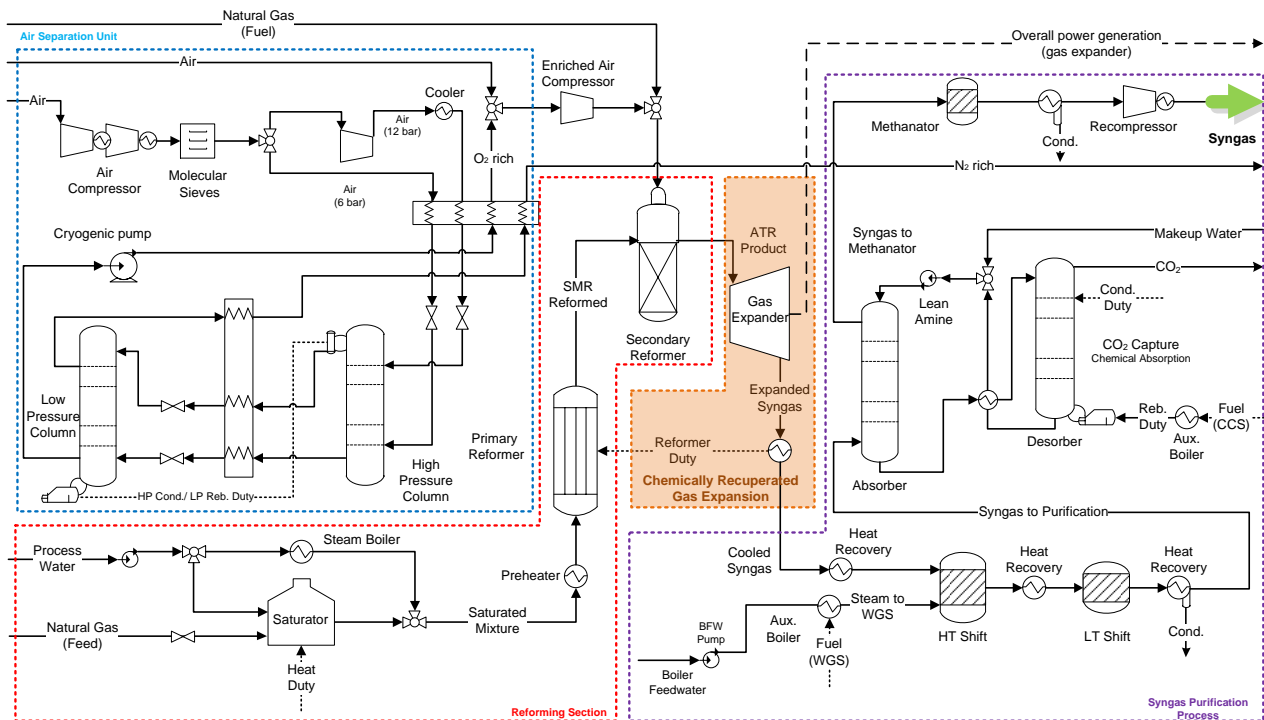


Fig. 2. Single Pressure, Chemically Recuperated Gas Turbine-based configuration (Single Pressure GT).

The next goal is to devise a means of further reducing the avoidable exergy losses, so that the actual process can approach the quasistatic operating conditions, but still maintaining the high process throughput. To this end, the Le Châtelier and the Counteraction principles can be used to counterbalance the clashing outcomes set off by simultaneously intensifying the chemical process yield rates (i.e. by increasing the driving force), whereas attempting to reduce the exergy losses (by reducing it) [26]. As stated by the Le Châtelier Principle, ‘any system in chemical equilibrium that is subjected to a variation in its concentration, temperature, volume, or pressure will try to adjust itself in order to *partly* reestablish the stable equilibrium conditions temporarily lost due to the change applied’ [24]. Thus, analogously to a heat exchanger network in which an increase in the temperature difference between the exchanging streams triggers an increase of the heat transfer rate, in a chemical reactor, the increase of the reactive driving force ( $-\Delta G$ ) may be caused by either (i) a decrease of the temperature of an exothermic reactor (or an increase of the temperature of an endothermic one); or (ii) an increase of the pressure of a decreasing-volume reaction (or a decrease of the pressure of an increasing-volume one). On the other hand, the exergy analysis can be used in conjunction with the Le Châtelier principle to work out means of minimizing the excessive driving forces, so that an improved exergetic performance can be achieved [25]. This is the essence of the Counteraction principle, which aims to minimize the large driving force in selected components without leading to negative results at the remaining stages of the overall system.

Consequently, the Counteraction principle [26] proves to be useful in identifying the best energy integration technologies depending on the nature of the energy transformations involved. For instance, since the reforming process relies on an increasing-volume, endothermic reaction that proceeds faster at higher temperatures, but whose equilibrium is favored at lower pressures, this process may be better performed at two decremental levels of pressure (Fig. 3) according to the Counteraction Principle. Furthermore, since the exothermic secondary reformer effluent is at much higher temperature than the level of temperature of the steam generation, the expansion of this stream previously to the heat recovery in the GHR and HRSGs is decidedly advisable in order to reduce the large driving forces associated to the heat transfer process. Thus, the integration of a dual pressure syngas production process based on the CRGT concept represents an interesting application for inquiring about the effect of the variation of not only the operating parameters (e.g. pressure, temperature and streams composition) but also the arrangement of the unit operations on the overall plant performance. It is worthy to notice that the layout proposed in Fig. 3 resembles the gas reheat process, already used in conventional gas turbine power systems and claimed to be a way to increase the power throughput without increasing the inlet temperature of the turbine [7, 8].

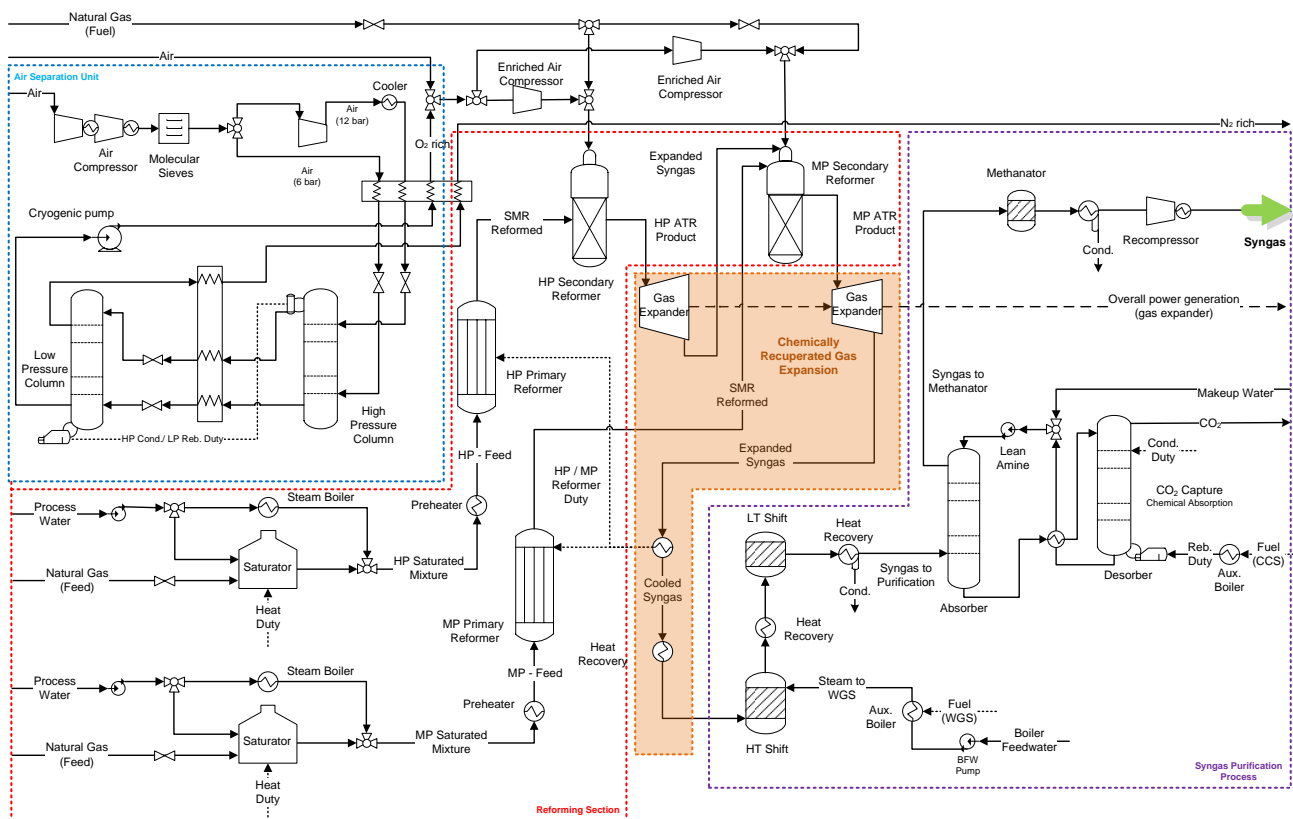


Fig. 3. Dual Pressure, Chemically Recuperated Gas Turbine-based configuration (Dual Pressure GT).

Finally, inspired by a suitable combination of the previous energy conversion approaches and aiming to improve the energy integration potential of the single and dual pressure CRGT-based syngas production plants, two additional configurations have been proposed (Fig. 4-5). In those approaches, a comprehensive steam network recovers the waste heat along the chemical process in order to generate part of the power supply as well as the process steam consumed in the reforming, shift reactions and syngas purification. Meanwhile, the utilization of the high temperature has

expander and the CRGT concept profits from the thermodynamic potential at higher temperatures, analogously to the classical application of a combined cycle. This improvement allows for a slight reduction of the fuel consumed, that otherwise would be burnt in auxiliary boilers. Moreover, as it will be shown, the configurations shown in Fig. 2-5 also entail a substantial reduction of the associated greenhouse gas emissions and the process irreversibility.

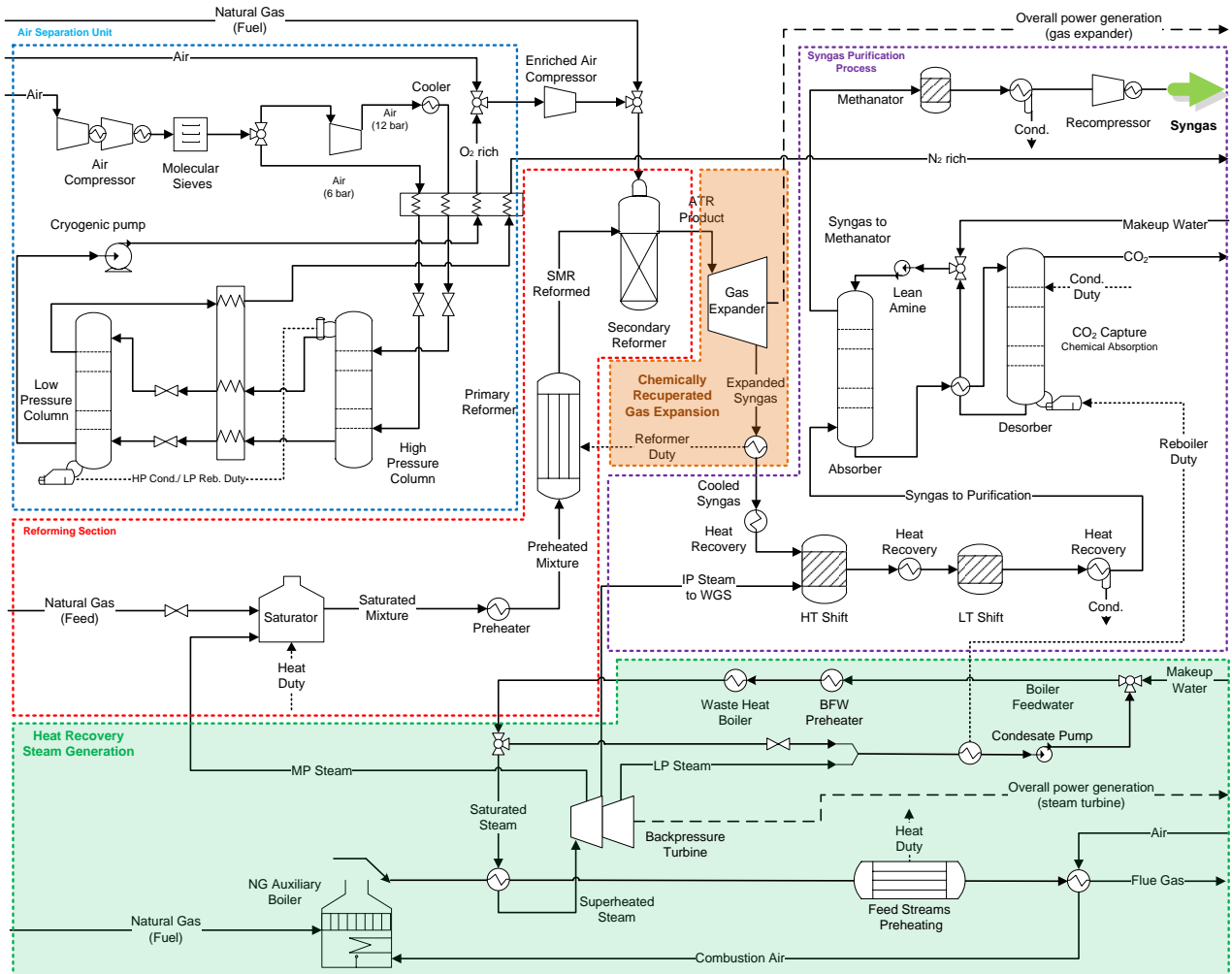


Fig. 4. Single Pressure, Chemically Recuperated Gas Turbine-based configuration with Steam Network (Single CC).



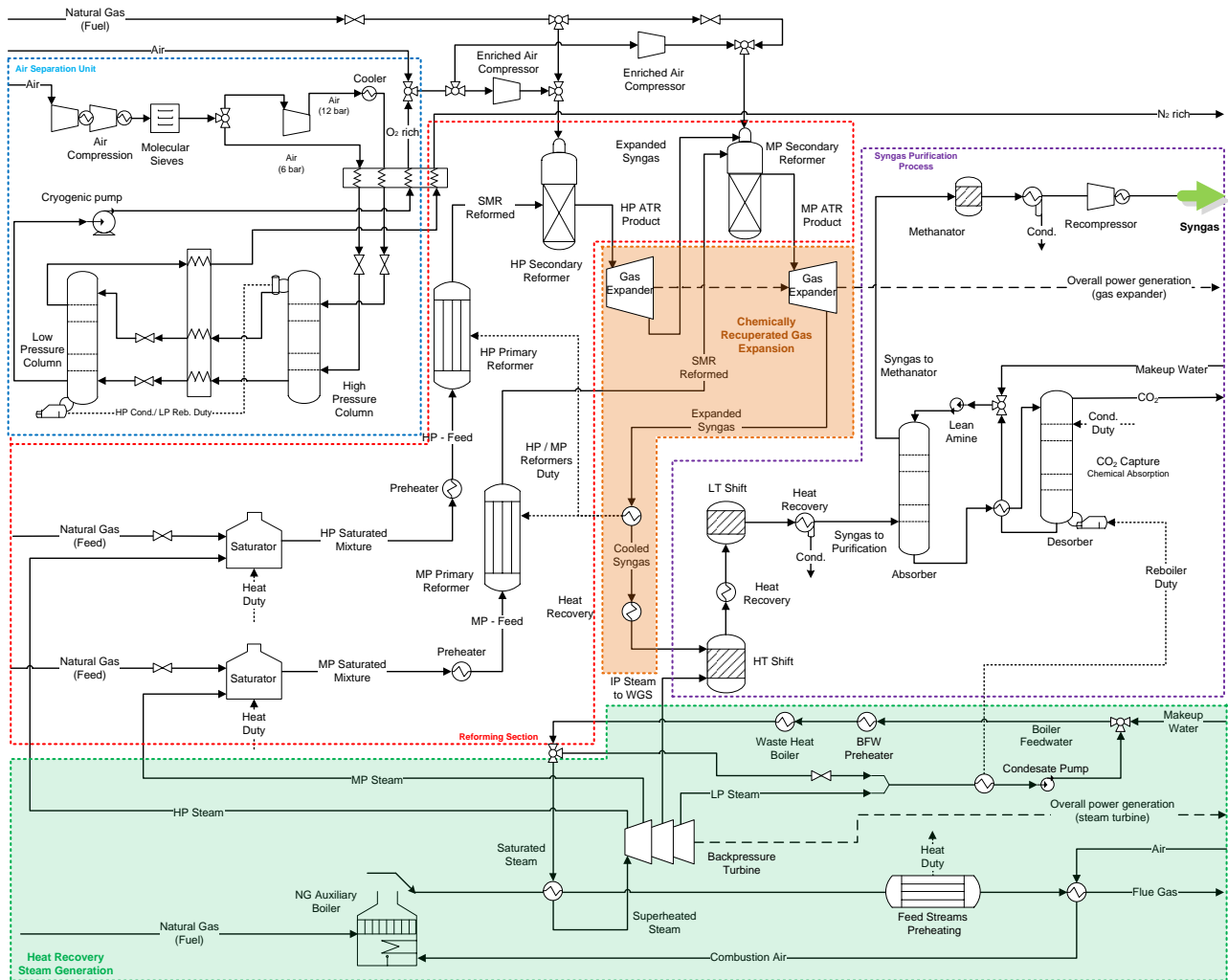


Fig. 5. Dual Pressure, Chemically Recuperated Gas Turbine-based configuration with Steam Network (Dual CC).

### 3. Methodology

In the last decades, several methods based on the First and Second Laws of Thermodynamics have been developed for defining indicators to assess the performance of chemical and industrial processes [27]. Since these Principles rely on observed physical laws, they can be used to predict the upper and lower bounds of the attainable optimal solution, regardless of the energy technology selected (top-notch, conventional) or the nature of the energy conversion achieved (reversible, irreversible, adiabatic). The energy integration (or *pinch* method) [28] and the exergy method [29] are among the most common thermodynamic methods used in the chemical plant diagnosis. In the former, the waste heat that otherwise would be irretrievably dissipated by the cooling system to the environment is minimized through the integration of the chemical plant to the utility system, not only reducing the consumption of costly external resources (e.g. fossil fuels) but also the wastes and emissions associated to them. Meanwhile, the aim of the exergy method is to identify the causes of the *irreversibility* (entropy generation) in the designed setups, so that the operation conditions can be adjusted in order to reduce the degradation of those resources. However, despite the relevance of the engineering heuristics and physical principles when building feasible configurations of chemical

plants, the designed setups may still operate anywhere amidst the upper and lower bounds of the feasible space of the independent variables. Thus, it is highly likely that they at most represent *local* optimum operating conditions in terms of one or more performance criteria adopted. In order to overcome this issue, other methods, based on *algorithmic* routines, aim to provide a more *systematic framework* that handles the synthesis of the process *flowsheet* as a *mathematical programming* problem. Thus, in this paper, a combination of the energy integration, exergy method and optimization tools is used to assess the performance of the various syngas production plants in terms of energy consumption, process irreversibility and environmental impact.

### 3.1. Process synthesis and optimization tools

The evaluation of the thermodynamic properties of each flow as well as the mass, energy and exergy balances of each unit operation are carried out by using Aspen Hysys® V8.8 software [30] and the semi-empirical Peng-Robinson equation of state. In the case of the chemical absorption unit, the Electrolytic Non-Random Two Liquid (ENRTL-RK) method is used for taking into account the strongly non-ideal liquid properties and the dissociation chemistry present in the reactive absorption-desorption systems. Firstly, several case studies have been performed to map the feasible window of the independent variables of the novel syngas production systems that guarantees the same production rates and syngas specifications of the conventional configuration. In this way, many configurations can be excluded from further investigation in early stages of design, largely reducing the extent of the search space. These results have been used as the initial input to a MS Excel® VBA Optimization framework developed by Sharma et al. [31] based on the Non-dominated Sorting Genetic Algorithm (NSGA)-II [32]. In order to further reduce the computational cost, a sequential quadratic programming (SQP) tool embedded in Aspen® Hysys is used to solve the optimization problem close to the global optimal predicted by the Genetic Algorithm.

### 3.2. Exergy analysis and exergy efficiency definition

Exergy is defined as the maximum available work that can be obtained from a thermodynamic system when it interacts with the environment by means of reversible processes until the mechanical, thermal and chemical equilibrium state with the components in the environment is definitively attained [29]. The total exergy Eq.(1) can be divided into its kinetic ( $B^K$ ), potential ( $B^P$ ), physical ( $B^{PH}$ ) and chemical components ( $B^{CH}$ ), however, the two latter, calculated by Eqs. (2) and (3), often overwhelm the kinetic and potential terms:

$$B^T = B^P + B^K + B^{PH} + B^{CH} \quad (1)$$

$$B^{PH} = H - H_o - T_o(S - S_o) \quad (2)$$

$$B^{CH} = N_{mix} b^{CH} = N_{mix} [\sum x_i b_i + R_u T_o \sum x_i \ln \gamma_i x_i] \quad (3)$$

where  $N_{mix}$  is the total molar flow rate of the stream (kmol/s),  $b^{ch}$  is the total specific chemical exergy (kJ/kmol),  $b_i$  is the standard chemical exergy of the component  $i$  in the mixture (kJ/kmol),  $x_i$  is the molar fraction of the component  $i$ ,  $R_u$  is the universal constant of the gases,  $\gamma_i$  is the activity coefficient,  $H$  and  $S$  represent the enthalpy (kW) and entropy flow rates (kW/K) of the substance, and the subscript  $o$  stands for the properties calculated at the environmental conditions, here considered as  $P_o = 1$  bar and  $T_o = 298.15$  K. Furthermore, the exergy balance of a control volume operating at steady state can be calculated by using Eq. (4):

$$\dot{B}_{dest} = \sum_{inlet} \dot{m} \cdot b^m - \sum_{outlet} \dot{m} \cdot b^m + \int \left(1 - \frac{T_o}{T}\right) \frac{\delta Q}{dt} - \dot{W}_{useful} \quad (4)$$

where,  $b^m$  is the total exergy of the mass streams going in and out of the control volume (kJ/kg),  $Q$  is the heat rate transferred through the boundaries of the control volume (kW), and  $W_{\text{useful}}$  is the actual amount of power that can be produced from the process analyzed (kW). Meanwhile, the term  $B_{\text{dest}}$  stands for the irreversibility occurred in the control volume of the industrial process studied (kW), namely a measure of the degradation of the thermodynamic potential of the exergy flows involved. Accordingly, the exergy analysis is a valuable tool that allows comparing the actual and ideal performances ( $B_{\text{dest}}=0$ ), constraining the search and design space of the technological developments to feasible thermodynamic solutions ( $B_{\text{dest}} > 0$ ). Furthermore, the exergy method provides a rational means of evaluating and comparing a variety of industrial processes in a more meaningful way as it indicates the quality of the energy conversion processes as well as the deviation from the environmental conditions. For this reason, the exergy method is generally used to define suitable indicators for industrial and chemical plants.

Table 1 compares two exergy efficiency definitions, Eqs.(5-6), proposed for better evaluating the overall performance of syngas production plants [22]. It must be noticed that, since the exergy of the input and output material flows are much larger than any other exergy flow rates, the *relative* exergy efficiency, Eq.(6) may lead to higher values. According to this, aiming to differentiate the exergy effectively transformed by the system from the untransformed exergy, the *consumed-produced* exergy efficiency is also calculated by using the exergy change of selected streams in the conversion processes. In other words, Eq. (5) aims to evaluate the extent at which the chemical exergy consumed in the process can be recovered in the form of an increased physical exergy of the products, while minimizing the system irreversibility. Evidently, the lower the surplus power produced and the higher the exergy recovered in the form of reformed mixture, the better the performance of syngas production. The *relative* exergy efficiency, in turn, determines the ratio between the minimum exergy required to materialize the syngas to the actual exergy consumption of the syngas production unit. Physical and chemical exergy calculations, as well as the exergy efficiencies are assessed by using VBA ® scripts as user defined functions [33].

Table 1. Plantwide exergy efficiency definitions of the syngas production systems.

Definition	Formula
ConsProd (5)	$\eta_{\text{ConsProd}} = \frac{B_{\text{Produced}}}{B_{\text{Consumed}}} = \frac{(B_{\text{outlet}}^{\text{PH}} - B_{\text{inlet}}^{\text{PH}}) + W^{\text{exported}}}{(B_{\text{inlet}}^{\text{CH}} - B_{\text{outlet}}^{\text{CH}})}$
Relative (6)	$\eta_{\text{Relative}} = \frac{B_{\text{Consumed, ideal}}}{B_{\text{Consumed, actual}}} = \frac{B_{\text{Syngas}}}{B_{\text{CH}_4} + B_{\text{BFW}} + W^{\text{import}}}$

B = exergy rate or flow rate (kW), PH: physical exergy, CH: chemical exergy, ConsProd: Consumed/Produced, BFW: boiler feedwater, Dest: destroyed.

### 3.3. Optimization problem definition

Syngas production units are designed in sophisticated ways in which the processes streams are interrelated through recycle operations and an intricate waste heat recovery network. Consequently, the numerous design variables involved not only make the search space large in

magnitude, but their interdependency renders the search for the optimality a complicated non-linear problem [34]. On the other hand, despite their powerfulness, the standalone application of the energy integration and exergy method may require of a considerable amount of trial and error to find solutions that are close to the predicted thermodynamic bounds [34]. In fact, the energy integration method (or *pinch* method), is based on the univocal determination of the initial and final temperatures as well as the variation of the enthalpy flow rate of each stream involved in the heat exchanger network (HEN). However, once the optimizer sets new values to the independent variables of the optimization problem, the simulator calculates updated values for the physical properties of the integrated streams. Consequently, a totally different HEN will be generated which, in turn, will have an important impact in the choice of the new values of the independent variables [35, 36]. Therefore, the originally defined set of temperatures and exchanged heat values become a set of variables that will depend on the global optimization problem [37]. Furthermore, it is expected that the isolated optimization of a major plant component be facilitated when strategically located at the frontend of the chemical process. However, for other major components located downstream in the production process, it cannot be automatically expected that, when optimized in isolation, the remaining components also operate in optimal conditions [34, 38, 39]. Thus, despite the fact that novel syngas production plants represent interesting applications for improving the performance of systems traditionally based on non-renewable resources, (i) the interrelation between the process parameters, (ii) the rearrangement of the new and the existing unit operations, as well as (iii) the perturbation of the combined steam and power production balances render the optimization of these systems a cumbersome task, were it not for a systematic optimization framework.

Fortunately, by separating the process flowsheet modeling from the heat integration problem, the calculation of the mass and energy balances and the simulation of the complex energy conversions can be handled by the modular simulation Aspen® Hysys, whereas the determination of the minimum energy requirements (MER) and the solution of the energy integration problem is performed by an additional Excel® platform. Meanwhile, an embedded SQP approach is used to find the optimal solution subject to the technical, thermodynamic and operational constraints presented in Table 2.

*Table 2. Optimization problem definition.*

<p><b>Objective functions:</b> Minimum Specific Exergy Destruction (~Minimum Specific Methane Consumption)</p> <p><b>Subject to the constraints:</b></p> <ul style="list-style-type: none"> <li>• No net power import. Preferably no net power export.</li> <li>• Maximum ATR catalyst temperature, 1,100°C for safe hydrogen operation, due to metallurgical limitations at high pressure and to avoid adverse effects on catalyst activity and lifespan.</li> <li>• Minimum and maximum primary reformer temperature 330°C-800°C for reasonable catalyst activity and methane conversion.</li> <li>• Minimum energy requirements satisfied by the waste heat recovery or by the utility system.</li> <li>• Maximum operating pressure of reformers, 35 bar.</li> <li>• Minimum steam to carbon ratio, <math>S/C = 2.5</math> to avoid carbon deposition.</li> <li>• No carbon oxide components in the purified syngas (ppm levels).</li> </ul>
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- Hydrogen production: 6,100 – 6,500 kmol/h
- Fresh syngas molar composition suitable for ammonia production,  $H_2/N_2$  ratio about >2.999, inerts content ( $CH_4 + Ar$ ) < 10%.

**Design Variables:**

- Steam to Carbon ratio, 2.5-6.0
- Primary reformer outlet temperature,  $T_{SMR}$ , 330-800°C.
- $CH_4$  fuel to feedstock ratio, 0.1 – 2.0
- Oxygen enrichment, 0 – 40%  $O_2$  in air
- Highest Reforming Pressure, 30-35 bar in both conventional and CRGT based configurations.
- Lowest Reforming Pressure (Expander outlet pressure for CRGT based configurations), 4 bar
- Split fractions (Enriched air,  $CH_4$  feed and  $CH_4$  fuel in dual pressure CRGT based configurations), 0.0 – 1.0
- Steam split fractions in the steam network (to superheating coil after saturation), 0.0 – 1.0
- Gas turbine bypass of the autothermal reactor effluent, 0.0 – 1.0
- Primary reformer bypass of the preheated reactants, 0.0-1.0
- Steam superheating temperature in the steam network, 380°C-500°C
- Steam to water gas shift reactors, 0-600 kmol/h
- Normal air molar flow rate, 1,000-4,000 kmol/h
- $CH_4$  feed molar flow rate, 1,000-2,000 kmol/h

**Constants:**

- Compression efficiency (85%). Expander efficiency (90%)
- Cooling water and boiler feedwater temperatures, 25°C
- Minimum temperature approach in the HEN (20°C).

## 4. Results and discussion

In this section, the performance of the conventional syngas production plant is compared to that of the plants based on the CRGT concept in terms of specific exergy consumption,  $CO_2$  emissions, exergy efficiency and specific exergy destruction in the various components.

### 4.1. Optimal operation conditions of the conventional and novel configurations

Table 3 summarizes the optimal process variables calculated for the five configurations of the syngas production plant, according to the optimization problem given in Table 2. It is worthy to notice that, since the high-grade hot utility has been used more efficiently in the CRGT-based syngas production plants, compared to the conventional configuration, the specific consumption of natural gas of the proposed layouts is slightly reduced (0.5-2.7%) whereas the cooling requirements also decrease (0.5-10.2 %). On the other hand, an increased air enrichment is required in the CRGT-based configurations in order to provide the minimum exergy heat necessary to carry out the endothermic reactions and supply the power demand. Some authors reported no benefits in terms of methane conversion in the ATR when an air enrichment beyond 34%  $O_2$  is used [40], although the recommended values range from 25 to 40%  $O_2$  in air [41, 42]. In any case, the extent of air enrichment must consider the maximum outlet temperature of the ATR and, preferably, should not

excessively produce CO<sub>2</sub> gas, since it will consume the valuable hydrogen in the downstream methanator system. Thus, it is expected that, for a given steam to carbon ratio, there exists an optimal oxygen to fuel ratio that results in the highest production of hydrogen [43, 44], and also fulfills the overall heat and power requirements of the process.

*Table 3. Main process variables of the syngas production facilities studied.*

Process parameter	Conventional	Single Pressure GT	Dual Pressure GT	Single Pressure CC	Dual Pressure CC
CH <sub>4</sub> feed (kmol/h)	1,800.0	1,150.0	1,085.0	1,349.0	851.9
CH <sub>4</sub> bypass to ATR feed (kmol/h)	274.7	1,202.0	1,247.0	893.0	1,364.0
CH <sub>4</sub> radiant fired furnace (kmol/h)	612.4	-	-	-	-
CH <sub>4</sub> auxiliary boiler (kmol/h)	-	450.0	403.4	535.1	439.4
CH <sub>4</sub> slip (kmol/h) <sup>1</sup>	87.1	77.1	148.9	100.1	118.6
H <sub>2</sub> production rate (kmol/h)	6,171	6,498	6,196	6,499	6,185
Spec. CH <sub>4</sub> cons. (kmolCH <sub>4</sub> /kmolH <sub>2</sub> )	0.4213	0.4194	0.4174	0.4119	0.4101
Air molar flow (kmol/h)	2,524	2,610	2,483	2,671	2,448
Oxygen rich molar flow (kmol/h)	440.0	919.9	911.9	578.4	718.3
Air enrichment (mol fraction)	30.01	36.86	37.35	31.82	34.80
Nitrogen rich molar flow (kmol/h) <sup>2</sup>	1,440	2,942	2,984	1,892	2,349
Steam to carbon ratio –HP	3.000	3.342	3.000	3.000	3.489
Steam to carbon ratio – MP	-	-	3.000	-	4.154
System Pressure – HP (kPa)	3,500	3,000	3,000	3,000	3,000
System Pressure – MP (kPa)	-	-	1,341	-	1,400
Exhaust Pressure – LP (kPa)	-	1,095	600	1,400	900
Cooling Requirement (kW) <sup>3</sup>	127,559	133,615	124,991	120,560	116,846
Spec. Cooling Req. (kJ/kmolH <sub>2</sub> )	74,411	74,022	72,619	66,777	68,007
Methane conversion (%)	96.76	99.58	96.68	96.39	98.67
Primary reformer outlet T (°C) - HP	700	728	730	800	519
Secondary reformer outlet T (°C) - HP	956	994	1089	1079	1052
Primary reformer outlet T (°C) - MP	-	-	330	-	769
Secondary reformer outlet T (°C) - MP	-	-	900	-	954
Enriched air split (% to HP line)	-	-	85.06	-	73.64
CH <sub>4</sub> feed split (% to HP line)	-	-	94.87	-	4.89
CH <sub>4</sub> fuel split (% to HP line)	-	-	77.19	-	93.03
CO <sub>2</sub> captured flow rate (kmol/h)	1,981	2,274	2,183	2,141	2,097
Spec. CO <sub>2</sub> captured (kmolCO <sub>2</sub> /kmolH <sub>2</sub> )	0.321	0.350	0.352	0.329	0.339
Spec. CO <sub>2</sub> captured (t <sub>CO2</sub> /t <sub>H2</sub> )	7.1	7.7	7.8	7.3	7.5
CO <sub>2</sub> emitted flow rate (kmol/h)	612.4	450.0	403.4	535.1	439.4
Spec. CO <sub>2</sub> emitted (kmolCO <sub>2</sub> /kmolH <sub>2</sub> )	0.099	0.069	0.065	0.082	0.071
Spec. CO <sub>2</sub> emitted (t <sub>CO2</sub> /t <sub>H2</sub> )	2.183	1.523	1.432	1.811	1.563
Water consumption (m <sup>3</sup> /h)	97.48	69.40	69.13	73.07	65.90
Condensate prod (m <sup>3</sup> /h)	57.93	40.86	34.65	32.47	29.02
CH <sub>4</sub> +Ar content (%) <sup>4</sup>	1.54	1.56	2.44	1.67	2.02
H <sub>2</sub> /N <sub>2</sub> ratio <sup>4</sup> molar	3.036	2.999	2.999	3.000	3.075

1. Methane slip in the product syngas can be recovered and recycled as fuel to the syngas production process; 2. 97.75% Nitrogen at 27°C, 110 kPa; 3. Cooling water 25-40°C, 60% relative humidity; 4. Ammonia loop feed inerts content CH<sub>4</sub>+Ar, and H<sub>2</sub>/N<sub>2</sub> ratio.

According to Fig. 6, the conventional configuration is not only responsible for the largest exergy consumption, but also for the highest specific CO<sub>2</sub> emissions. Additionally, depending on the effectiveness and the amount of coils in the HRCT, the flue gases leaving the furnace stack might be rejected to the environment when a relatively large amount of exergy could be still profitable to preheat cold process streams [45, 46]. Moreover, the flue gases from the fired furnace are close to atmospheric pressure and, as such, they are not suitable for directly producing power. Instead, they are used for steam superheating as well as for preheating feed streams. Consequently, the reduction or the elimination of the firing in the primary reformer furnace, by means of a bypass of methane to the secondary reformer, may offset the flue stack losses and the emissions associated to that technology.

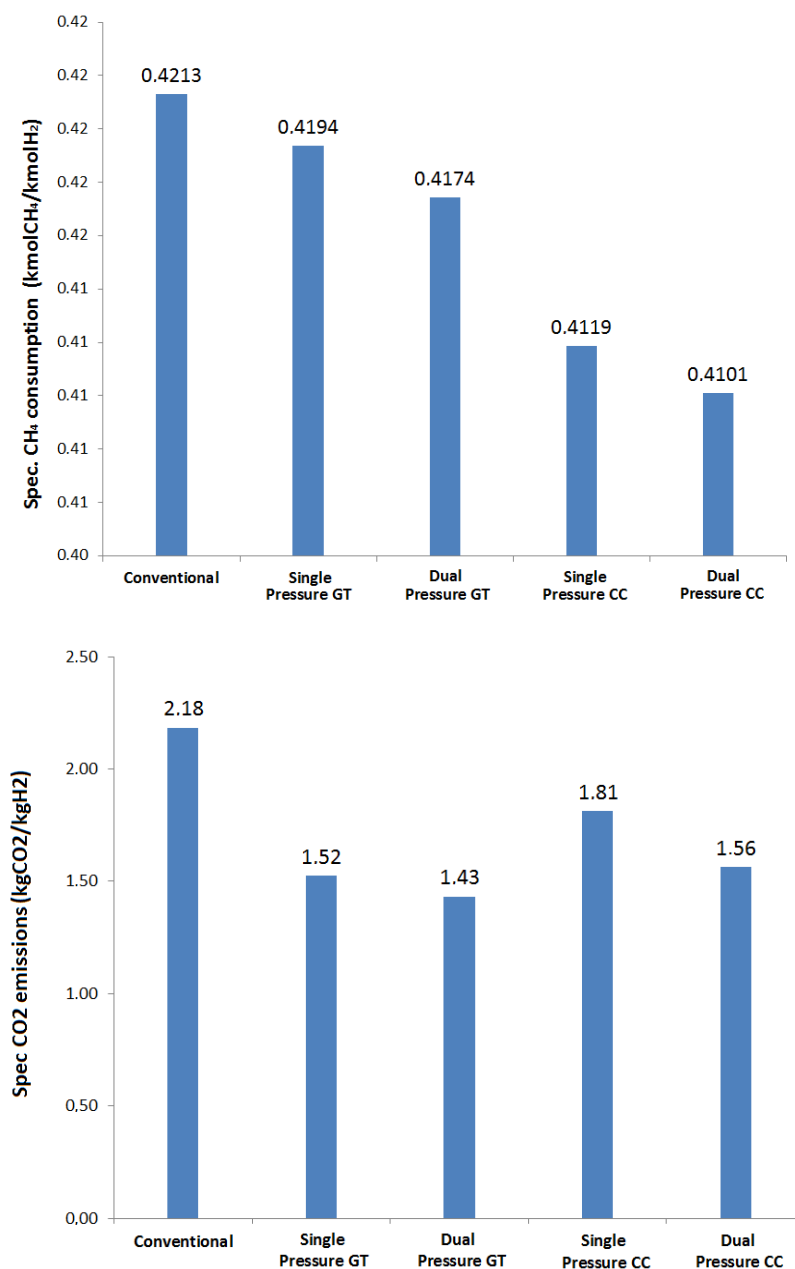


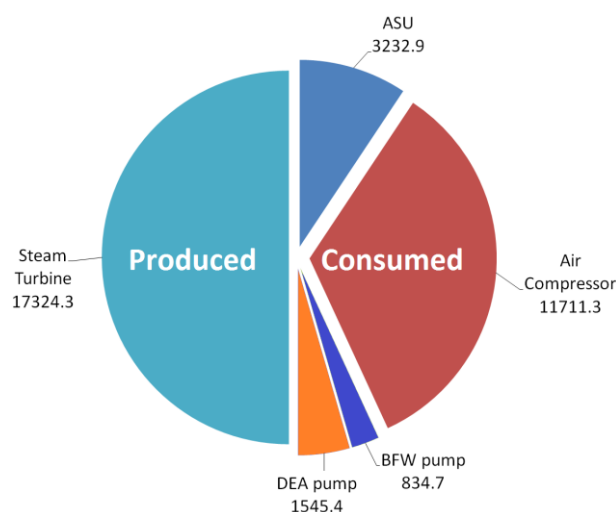
Fig. 6. Comparison between the specific exergy consumption (above) and specific CO<sub>2</sub> emissions (below) of the syngas production configurations.

Meanwhile, in the CRGT-based configurations, the pressurized gases exiting from the adiabatic ATR reactor are readily expanded for producing power right before any heat exchange process may take place. Moreover, unlike the conventional design, the duty of the gas heated reformer is supplied by a gaseous mixture at higher pressures [47, 48]. These features entail desirable operating conditions that partially enable to overcome the main disadvantages of the conventional primary reformer. Actually, in the conventional design, the maximum pressure differential and allowable heat flux across the reformer tubes are set by the mechanical and metallurgical restrictions. For this reason, the tube diameter cannot be arbitrarily enlarged, entailing also a restriction to the revamp of the conventional plant. In practice, the primary reformer currently poses the most critical bottlenecks that hinder the development of the so-called MEGAMMONIA® plants [49]. Fortunately, the proposed configurations shown in Figs. 2-5 ensure a good heat transfer performance and reduce the pressure differential across the catalytic tubes, thus, increasing the process reliability. As it can be also seen from Table 8.3, in the case of the dual pressure configuration with gas expansion only (i.e. Dual Pressure GT), the entire primary reforming process as well as most of the enriched air-blown partial combustion of the reformed mixture and the additional methane feed occur at higher pressures. Meanwhile, the medium pressure ATR is used to further convert the slipped methane from the HP reformers. The medium pressure ATR also reheats the expanded MP gas in order to increase the power generation, without exceeding the maximum allowable catalyst temperature in the ATR. However, when a steam network is integrated to the dual pressure configuration (i.e. Dual Pressure CC), the largest share of partial oxidation is still performed at the highest temperature and pressure, but most of the primary reforming is performed at medium pressure and lower temperature. This can be explained by a higher mechanical power required from the HP gas expander of the Dual Pressure GT configuration, due to the lack of an integrated waste heat recovery steam network (compare Figs. 7c and e). In other words, as long as an alternative technology of power generation relieves the load on the HP gas expansion system, the methane reforming is preferably addressed at a less equilibrium-limited, i.e. a lower pressure operating condition.

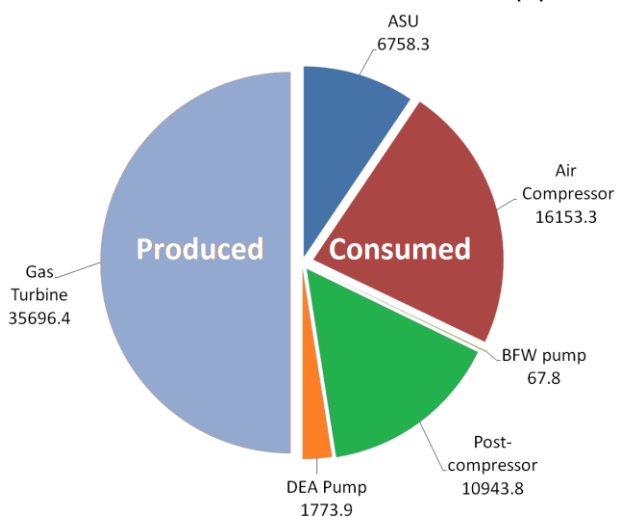
Although in the CRGT-based configurations an appreciable amount of fuel is still required by the auxiliary boiler, this consumption is about 12.1-34.6% lower than the fuel consumed in the fired furnace of the tubular reformer, due to a higher extent of partial oxidation achieved in the exothermic ATR. Furthermore, since the CO<sub>2</sub> produced by partial oxidation in the ATR is at a higher concentration, the capture process is facilitated compared to the challenging post-combustion carbon capture from the flue stack gases leaving the furnace of the externally fired primary reformer. As a result, the specific CO<sub>2</sub> emissions to the atmosphere in the conventional scenario (approx. 2.2 t CO<sub>2</sub>/t H<sub>2</sub>) are 21.5-52.4% higher than those obtained for the CRGT-based configurations (see Fig. 8.6). Furthermore, regarding the reduced water demand in the CRGT-based systems, it can be explained by the reduced S/C ratios necessary in the ATR compared to the excess steam required in the conventional tubular reformer. Furthermore, it is important to highlight that in the CRGT-based configurations, an additional amount of water vapor is produced at high pressure in the ATR through partial oxidation. In this way, the surplus water produced at higher temperatures and pressures in the ATR serves not only as a means of temperature control, but also as additional process feedstock as well as working fluid, unlike the water vapor present in the stack gases.



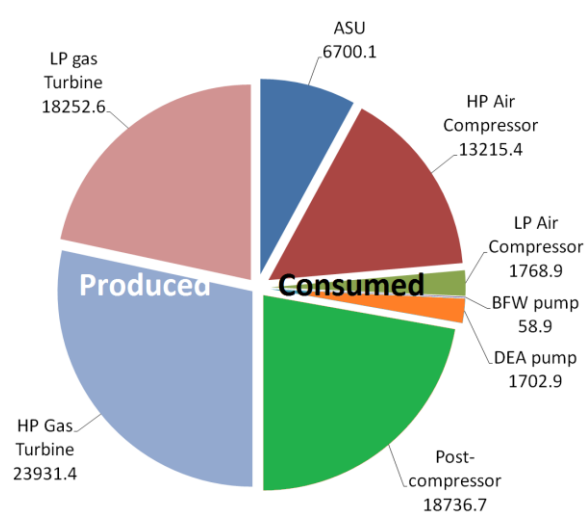
Finally, Figs. 7a-e details the distribution of the power generated among the various consumers in the syngas production plants analyzed. Certainly, since no net export is aimed, the optimal solution determines the operating conditions that minimize the surplus power and maximize the hydrogen yield. It must be also born in mind that, differently from the conventional case, the CRGT concepts rely on the expansion of the pressurized ATR effluent. This features renders necessary the recompression of the syngas produced up to the original ATR outlet pressure after the excess water is removed. According to Fig. 7b-e, the share of power consumption of the post-compression can be as high as 40% of the overall power demand and, in some cases, it even surpasses the air compression duty, whereas the third largest consumption comes from the energy intensive air enrichment unit (20%) and the amine circulation pump (10%).



(a) Conventional



(b) Single Pressure GT



(c) Dual Pressure GT

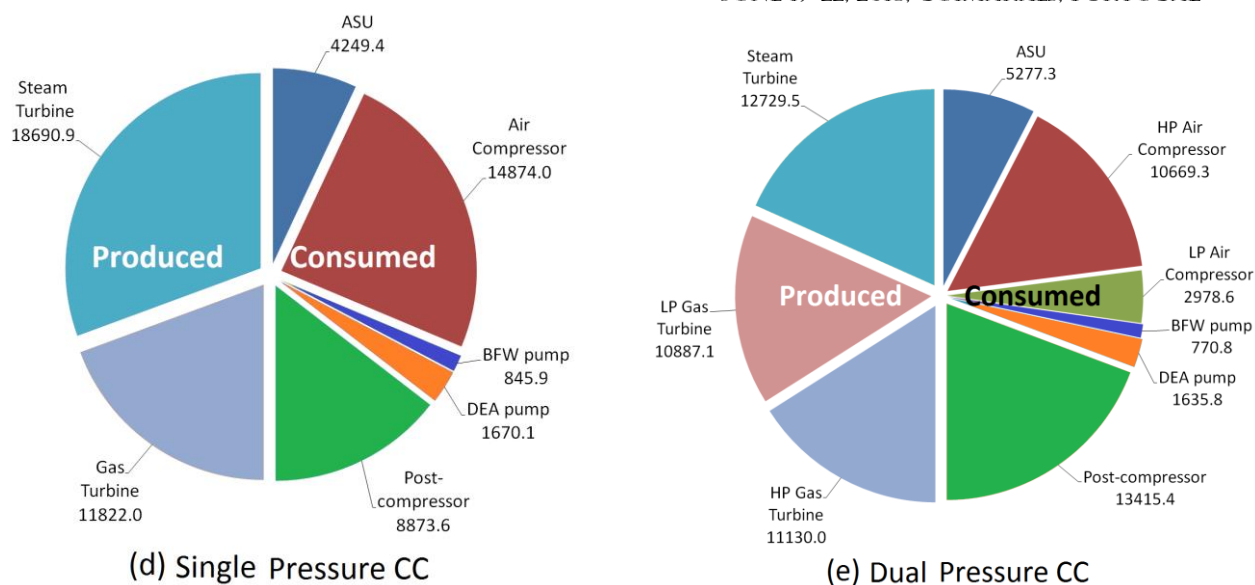


Fig. 7. Distribution of the power supply and demand (in kW) for the (a) conventional, (b) single and (c) dual pressure GT, and (d) single and (e) dual pressure CC configurations.

## 4.2. Energy integration and Carnot Grand Composite Curves.

Figure 8 show the Carnot Grand Composite curves (CGCC) of the conventional and CRGT-based syngas production plants reported in Table 3. As discussed in previous chapters, the area enclosed between the vertical axis and the CGCC represents the exergy destroyed in the heat exchanger network. According to Fig. 8, in the conventional configuration, a fraction of the exergy of the high-grade hot utility provided by the fired furnace is wastefully transferred to the environment. Actually, the flue stack gases leaving the convection train lead to an exergy loss equivalent to 6 MW, due to the practical limitations to fully recover this exergy. In contrast, in the CRGT-based configurations, the physical exergy of the excess reforming steam and the water produced by partial oxidation is mostly recovered up to its condensation [5].

According to Fig. 8, in all the configurations, an auxiliary boiler is still needed so that the total heating requirement for the steam generation can be balanced. However, regarding the CRGT-based configurations with gas expansion only (i.e. single and dual pressure-GT), the consumption of the chemical exergy of the fuel to merely produce steam suppose an avoidable exergy loss in the system. Effectively, the exergy destruction can be further reduced by integrating a heat recovery steam network, i.e. through the utilization of single and dual pressure-CC configurations. The resulting CGCCs (Fig. 8, right) resemble the combination of the conventional and the '-GT' profiles (Fig. 8, left). As a result, the plantwide and the cogeneration exergy efficiency increase compared to the conventional syngas production unit based only on heat recovery steam network [22].

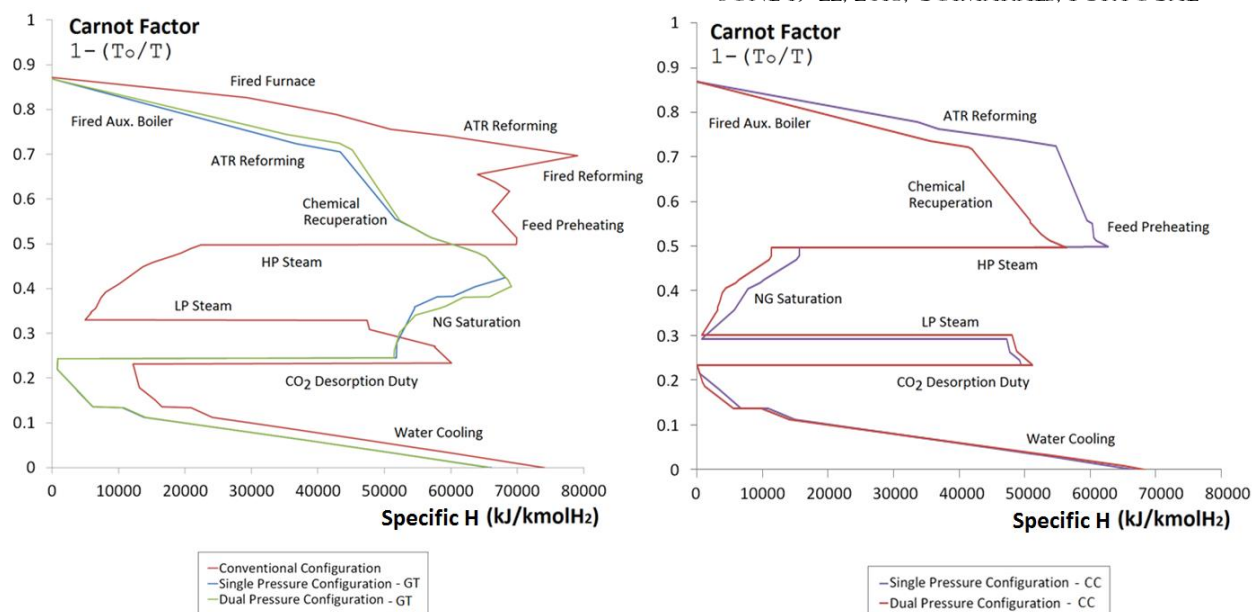


Fig. 8. Carnot Grand Composite curves (CGCC) for the conventional, single and dual pressure GT configurations (left) and for single and dual pressure CC configurations (right).

Clearly, in the case of the CRGT-based configurations, the integration of an additional steam network entails a trade-off between the *chemical recuperation* and the combined steam and power generation. In fact, since the exergy available from the ATR effluent is used for power generation and heating the GHR, the plantwide steam and power balance is drastically affected [41]. Some authors suggested that this is actually a great opportunity to involve cheaper, more readily available resources such as coal, or even less pollutant resources, e.g. biomass, in order to supply the energy for the steam generation. The import of ‘cleaner’ electricity from the grid, may be also considered, obviously depending on the mix and the cost of the electricity [50]. In this way, further alternatives for reducing the large driving forces and the environmental impact triggered by the utilization of the auxiliary boiler can be endeavored. For example, the diversification of the supply chains of the syngas and hydrogen derivatives, traditionally dominated by non-renewable energy resources.

### 4.3. Exergy performance of the conventional and proposed syngas production units.

Figure 9 shows the *relative* and *consumed-produced* exergy efficiencies calculated for the syngas production plants, as defined in Eqs. (5-6). Since the *relative* efficiency has been defined by using the minimum theoretical exergy consumption required to produce syngas from the elements of the environment, it accounts for the maximum potential of exergy savings. However, due to the large mass flow rates of the bulk chemical production process [51], the *relative* exergy efficiency is less sensitive than the *consumed-produced* counterpart.

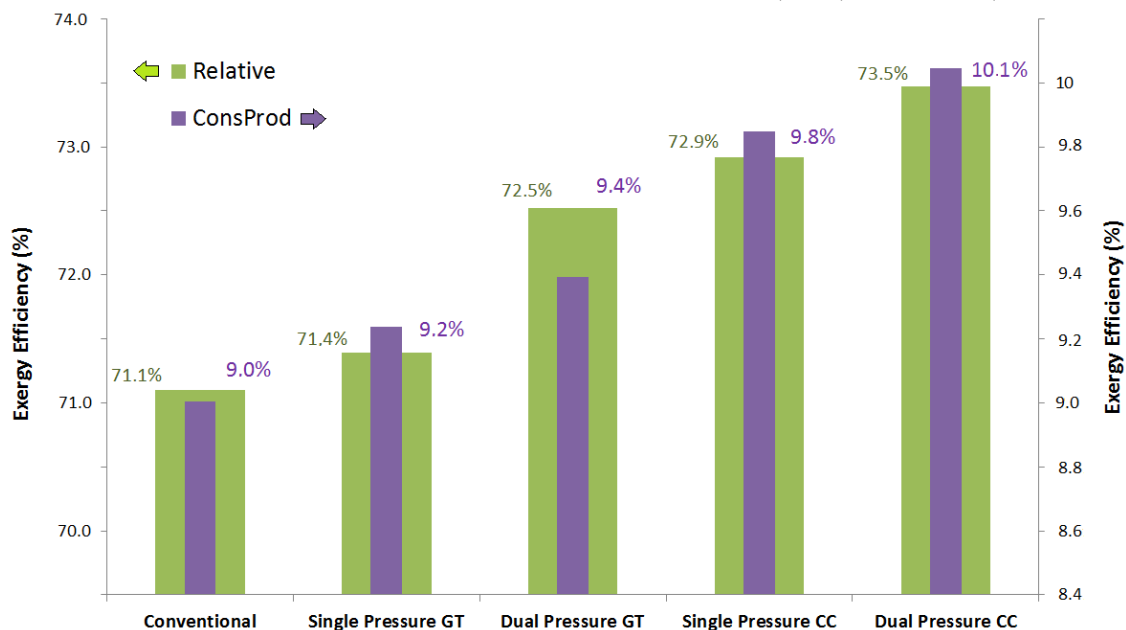


Fig. 9. Plantwide exergy efficiency of the syngas production plants studied.

As a result, the *consumed-produced* exergy efficiency (9-10%) is a more suitable indicator for determining the overall plant performance, along with the cogeneration exergy efficiency (Fig. 10) and the specific exergy destruction (Fig. 11). As expected, the higher degree of energy integration between the utility system and the chemical processes in the CRGT-based configurations leads to an increased efficiency of the respective cogeneration systems. According to Fig. 10, the integration of a chemically recuperated gas turbine concept with reheat together with an extensive heat recovery steam network (i.e. Dual Pressure CC) achieves a cogeneration efficiency of 55%, typical for a combined cycle. This value is 67% higher than that of the single pressure-GT configuration, analogous to a standalone open cycle gas turbine (OCGT). The capitalization on the other plant byproducts, such as the marketable CO<sub>2</sub>, potentially used in an associated urea or methanol, should be also included in the evaluation of the process efficiency.

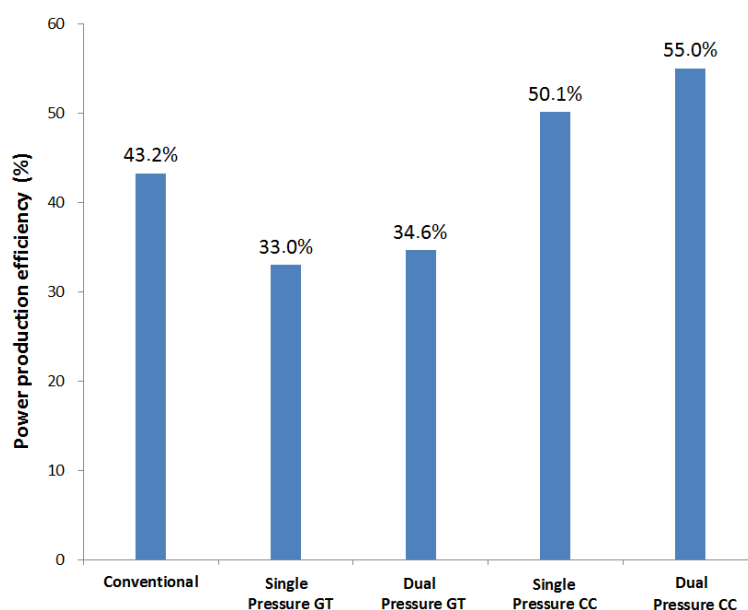


Fig. 10. Exergy efficiency of the integrated cogeneration systems in the syngas production plants.

Figure 11 compares the specific exergy destruction obtained for the studied configurations, which evidences that the higher the specific consumption, the higher the specific exergy destruction. Certainly, an increased fuel consumption often entails a worse utilization of the available resources to produce the same amount of product [5]. This explains an increase of 3-12% of the specific exergy destruction in the conventional system, compared to the CRGT-based configurations.

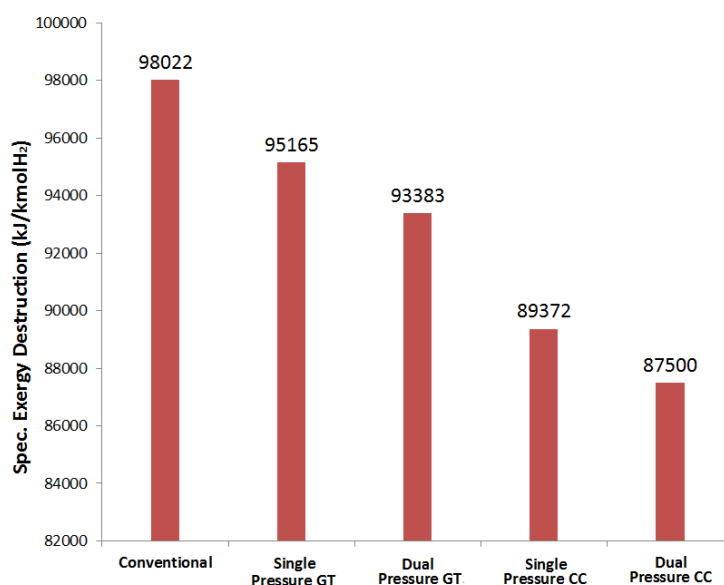


Fig. 11. Specific exergy destruction (kJ/kmol<sub>H2</sub>) for the studied syngas production plants.

Finally, Fig. 12 shows the distribution of the overall exergy destruction among the components of the conventional syngas production process. As it can be seen, the largest shares of exergy destruction correspond to the waste heat recovery steam network and the HRCT of the primary reformer, together accounting for 60% of the exergy destroyed in the conventional system. If both primary and secondary were also included, the share of exergy destruction increases up to 80% of the total irreversibility.

Figure 12 also shows the exergy destruction breakdown of the most representative components of the syngas production plants based on the CRGT concept. It is worthy to notice that, in all the studied plants, the share of exergy destroyed in the reforming sections is relatively similar. Furthermore, the auxiliary boiler used in the CRGT-based configurations represents about 40% of the whole irreversibility. Also according to Fig. 12, the exergy destruction share associated to the reformers in the dual pressure CRGT-based configurations is effectively reduced (3-21%) compared to the single pressure CRGT-based systems. This is owed to the application of the counteraction principle by operating the reforming sections at decremental levels of pressure [26]. Nevertheless, it is worthy to highlight that, in the optimal solutions, the lowest gas expansion pressure is not necessarily the atmospheric one, but rather an intermediate pressure. Indeed, higher operation pressures in the syngas production may lead to the reduction of the power consumption in the downstream syngas compressor train installed at the backend ammonia loop [41]. In practice, the natural gas supply is guaranteed at high levels of pressure, thus it seems to be preferable to maintain the operating conditions of the syngas production at higher pressures. Other benefits of an increased

operating pressure in the overall plant include smaller reactors, better ammonia conversions, as well as improved refrigeration and separation conditions.

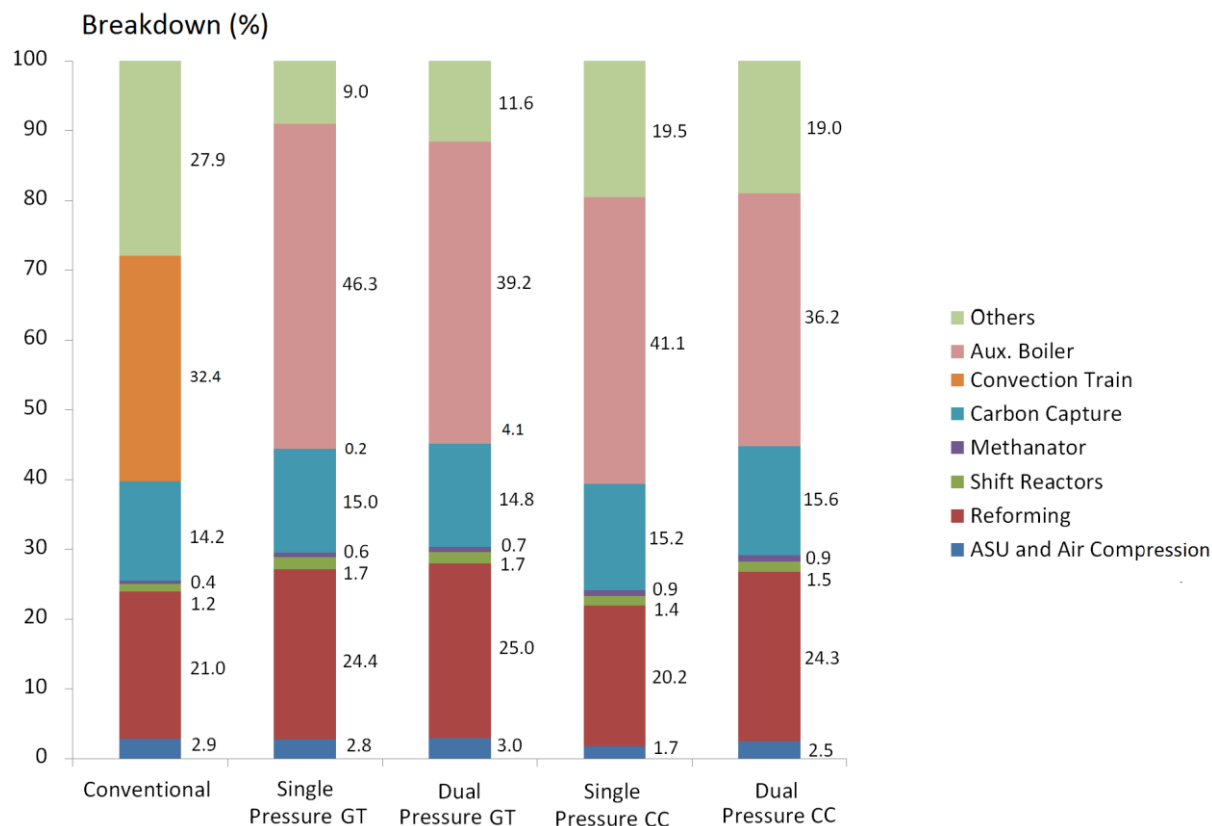


Fig. 12. Exergy destruction breakdown for representative components of the studied syngas production plants.

Some approaches found in the literature are in the same line of thinking of the subject presented in this chapter. As mentioned earlier, the partial oxidation gas turbine (POGT) simultaneously produces power and a secondary fuel that usually is a hydrogen-rich gas, which renders it well suited for the coproduction of power and chemicals. In this way, like the POGT systems, the configurations proposed here may also provide a secondary fuel that can be burned in a bottoming cycle (a cogeneration steam cycle, for instance) [52]. Moreover, according to some studies [53], the working fluid (*fuel gas*) provided by the partial oxidation reactor has a much higher specific heat than the complete combustion products. Thus, from an operational and thermodynamic point of view, more energy per unit mass of fluid can be extracted from the POGT expander compared to the typical gas turbine systems. As a result, a much smaller compressor is required, one that typically supplies less than half of the air flow required in a conventional gas turbine [52]. Other desirable features such as the ultra-low NO<sub>x</sub> emissions are also shared with the steam injected gas turbine systems.

Thus, as a motivation for future research works, non-conventional approaches will be worthy to explore, considering the limited room for improvement in the reactive components. Actually, the energy-intensive nature of the current technical process is mainly due to the large amount of exergy consumed in the process air enrichment and compression, syngas recompression, the steam generation in auxiliary boilers and the carbon capture systems, from which the highest potential of

exergy saving are expected [5]. Moreover, it has been also shown that the modification of the chemical process layout impacts the whole system irreversibility and allows for the minimization of the amount of exergy consumed in the syngas production unit. In this way, all the proposed novel configurations prove to be relevant in order to identify the opportunities of improvement in the syngas and hydrogen production systems. It is nevertheless important to point out that further economic evaluations should be performed in order to determine the marginal investment and risk cost involved [54]. However, exergy efficiency is not less important even at a cheaper natural gas cost scenario, because higher efficiencies are associated to smaller units and utility requirements, thus less operating costs, not to mention the striking reduction of the CO<sub>2</sub> emissions achieved [5].

## 5. Conclusions

Five different configurations, namely a conventional syngas production system and four proposed configurations based on the chemically recuperated gas turbine (CRGT) concept have been compared in terms of the minimum specific exergy destruction rate, the plantwide and cogeneration exergy efficiency and atmospheric CO<sub>2</sub> emissions. As a result, the physical reconfiguration of the chemical plant layout is shown to greatly reduce the driving forces and, thus, the irreversibility arisen from the combined heat and power production (CHP) system, but more importantly, the net CO<sub>2</sub> emissions. Actually, the proposed single and dual pressure configurations presented a specific exergy destruction ranging from 87.5 to 95.2 MJ/kmolH<sub>2</sub>, 3-12% lower than those found for the conventional process. Moreover, the exergy fuel consumption in the proposed CRGT-based configurations has been estimated as 0.5-2.7% lower than in the conventional design. Meanwhile, the cooling requirement in the proposed setups is substantially reduced (up to 10%) compared to the conventional plant. However, the most striking characteristic of these proposed setups has been their capability of cutting down up to 25% the specific atmospheric CO<sub>2</sub> emissions, compared to the conventional case. Thus, by optimally integrating a waste heat recovery steam network and a CRGT concept to the dual pressure syngas production system, the reacting driving forces in the reforming sections and the consumption of high-grade utility streams (e.g. chemical exergy of the fuel) can be reduced. To the author's knowledge, similar approaches has been proposed for expanding the exothermic reactor effluents, but none of them have integrated the CRGT concept to the chemical and cogeneration plant in a same physical structure. Advanced energy integration approaches that allow for increased waste heat recovery and improved cogeneration are unfortunately not customary practices in the conservative chemical and industrial sector. However, due to the reduced room for the energy consumption cutdown and, thus, an overall efficiency increase, the exploration of breakthrough approaches for energy conversion technologies, arrangements and energy resources become necessary, at least for elucidating the truly thermodynamic and technological potentials available in modern ammonia production facilities. Clearly, the minimization of the exergy destruction is not a priori an economic criterion, since this task is often achieved at the expense of additional capital investments. However, exergy efficiency is not less important, since higher efficiencies are associated to smaller units and utility requirements [5], not to mention the striking reduction of the CO<sub>2</sub> emissions, useful in growing credit carbon economies. It is thus necessary to further discuss the relationship between the overall exergy destruction, its distribution throughout the chemical process and the economy thereof. Meanwhile, the pursuit of the decarbonization of the syngas and hydrogen production sector will remain an active and open field of research.



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