Hydrogen intensified synthesis processes to valorise process off-gases in integrated steelworks

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Abstract. Integrated steelworks off-gases are generally exploited to produce heat and electricity. However, further valorization can be achieved by using them as feedstock for the synthesis of valuable products, such as methane and methanol, with the addition of renewable hydrogen. This was the aim of the recently concluded project entitled “Intelligent and integrated upgrade of carbon sources in steel industries through hydrogen intensified synthesis processes (i³ upgrade)”. Within this project, several activities were carried out: from laboratory analyses to simulation investigations, from design, development and tests of innovative reactor concepts and of advanced process control to detailed economic analyses, business models and investigation of implementation cases. The final developed methane production reactors are, respectively, an additively manufactured structured fixed-bed reactor and a reactor setup using wash-coated honeycomb monoliths as catalyst; both reactors reached almost full CO₂ conversion under slightly over-stoichiometric conditions. A new multi-stage concept of methanol reactor was designed, commissioned, and extensively tested at pilot-scale; it shows very effective conversion rates near to 100% for CO and slightly lower for CO₂ at one-through operation for the methanol synthesis. Online tests proved that developed dispatch controller implements a smooth control strategy in real time with a temporal resolution of 1 min and a forecasting horizon of 2 h. Furthermore, both offline simulations and cost analyses highlighted the fundamental role of hydrogen availability and costs for the feasibility of i³ upgrade solutions, and showed that the industrial implementation of the i³ upgrade solutions can lead to significant environmental and economic benefits for steelworks, especially in case green electricity is available at an affordable price.

Keywords: process-off gases valorization / hydrogen use / methane synthesis / methanol synthesis / advanced control / steelmaking industry sustainability / steel / carbon capture and usage

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1 Introduction

Industry and society as a whole are increasingly aware of the big challenges to be addressed to counteract climate change, whose impacts are already evident all over the world [1].

Although the basic role of Green House Gases (GHG) emissions to climate change was known from some decades, not enough actions were carried out until some years ago. On the other hand, an intensive increase of resources demand leads to primary materials scarcity, which, coupled to international energy crisis due to political factors, raises production costs.

Therefore, programs have been launched by European Union (EU) to be active in the fight against climate change and to confirm EU leadership in production of C-lean products and support to a sustainable society. The most important ones are the European Green Deal (EGD) and the more recent REPowerEU, respectively, to make Europe climate neutral by 2050 through an intensive promotion of decarbonisation, and to ensure more affordable, secure, and sustainable energy.

Steel industry is among the industrial sectors that are affected by these initiatives and committed to decarbonisation, reduction of GHG emission and optimization of resource and energy exploitation [2,3]. The Steel sector is indeed responsible of 7-9% of the whole anthropogenic CO₂ emissions [4] and, in the case of EU, it accounts for 22% of industrial CO₂ [5]. Considering the two main steel production routes (i.e., integrated and electric routes), the integrated route is responsible for about 87% of CO₂ emissions [6] associated to steel production and, therefore, shows the largest CO₂ mitigation potential.

Beyond the different steelmaking research works aimed at the substitution of fossil carbon and fuel with hydrogen both for reduction and heating purposes such as in [7,8], the optimal and flexible management and valorisation of Process Off-Gases (POGs) is receiving a consistent interest in the technical and scientific community especially because it can be a good option during the transition stage towards completely carbon-lean processes. POGs are intensively produced during the different transition stage towards completely carbon-lean processes. POGs are intensively produced during the different steelmaking production steps, and considering the integrated route, the main POGs are Coke Oven Gas (COG), Blast Furnace Gas (BFG) and Basic Oxygen Furnace Gas (BOFG).

Their composition makes them suitable to be valorised both energetically and chemically. Currently, POGs are generally exploited to produce heat and electricity to satisfy the internal demands [9] and different research works on this topic can be found in literature for the optimisation of POGs distribution for thermal and energetic usage [10–12].

However, POGs, that are carbon-rich by-products, can provide valuable products (e.g., methane and methanol) by obtaining environmental and economic benefits arising from an improved balance between revenues and costs related to CO₂ capture [13].

Methane plays an important role in steel production in the form of fossil Natural Gas (NG), since 11% of the energy consumed is derived from NG [14]. Thus, the production of methane from POGs can decrease the needs of fossil NG.

As mentioned in [9], the use of steelworks POGs to produce methanol was already investigated some decades ago [15,16], but technologies were not yet mature enough to raise industrial interest. Nowadays, being this technology included in Carbon Capture and Utilization (CCU) methodologies, it is receiving increasing interest in the scientific and industrial community. In the steelmaking field some noticeable techno-economic analyses have been recently carried out [17–20].

On the other side, an interesting preliminary investigation on methane synthesis from steelworks POGs is discussed in [21]. However, these works are mostly conceptual, being focused only on the use of some gases and not considering flexible and transient operations. Indeed, both methane and methanol synthesis processes are at the moment designed for large scale, steady-state operation and require almost stable stoichiometry of feed gases; hence, they are not suitable to operate with steelworks POGs, which are characterized by intermittent production (i.e., BFG), variable composition and competitive internal demand.

The present paper provides an overview of the activities and main outcomes of the recently concluded project entitled “Intelligent and integrated upgrade of carbon sources in steel industries through hydrogen intensified synthesis processes (i^3upgrade)” [22]. In particular i^3upgrade aimed at:

- providing flexible reactor concepts for directly upgrading steelworks off-gases with varying composition, availability and quality (transient operation);
- optimizing operation schemes and POGs valorisation opportunities by means of innovative advanced process control techniques considering also dynamic constraints of the integrated steelwork processes and of electricity grid services;
- enabling CO₂ savings by integrating the usage of renewable hydrogen from volatile power sources.

To sum up, the challenge was to provide more flexibility to steelworks off-gases management and to go beyond the state of the art of process conversion of carbon oxide off-gases.

The paper is organized as follows: Section 2 is dedicated to the preliminary analyses on POGs features and investigations on the integration of synthesis units into steelworks; Section 3 is focused on the developed and tested reactors, and dispatch controller (DC); Section 4 describes cost analyses, techno-economic scenario investigations, business models and implementation strategies. Finally, Section 5 provides concluding remarks.

2 Preliminary analyses and investigations

The average reference steelworks POGs composition is reported in Table 1.
POGs are mainly composed by COx (especially CO), H2 and N2. COG is rich in hydrogen and methane; it is, thus, the more suitable to thermal and heating purposes. BFG and BOFG, due to the high amount of CO and CO2, hold a lower caloric value with respect to COG, due to the higher inert contents, and can be exploited for methane and methanol syntheses after H2 enrichment.

Dedicated analyses of POGs bottled during steelworks operations were carried out to analyse trace compounds. Most of them are known poisons for the methane and methanol synthesis catalysts such as sulfur compounds and halides, whose content in BFG is reported in Table 2. Therefore, dedicated additional gas cleaning system are necessary before using the POGs in syntheses reactors. A gas cleaning scheme was proposed in [23] including: particle filter, halogen sorbents, hydrodesulfurization (HDS) reactor for the conversion of sulfur compounds and COS in H2S that is removed in a sorption bed containing metal oxides, a guard bed to protect the reactors by capturing escaped impurities, and a water removal unit.

Other possible POGs impurities are alkali metals, alkaline earth metals and iron, whose influence on catalytic activity of CuO/ZnO/Al2O3 was investigated in [24]. Metals reduce the number of active sites, but no modification of catalyst nature was observed. Sodium deviates from this behavior, and its strong basicity leads to stronger binding of CO2 on the catalyst surface. For this reason, further gas cleaning steps with respect to the above-listed ones should be considered based on concentrations of metals.

A preliminary investigation of hydrogen intensified methanation and methanol syntheses in integrated steelworks (Fig. 1) was conducted through simulations.

Dedicated models made it possible to investigate the integration of hydrogen intensified methanation and methanol syntheses [23] by also considering different hydrogen production processes [25]. Hydrogen enrichment is fundamental for BFG and BOFG to reach Stoichiometric Numbers (SN) values suitable to ensure high production yield of methane and methanol, as follows:

$$\text{SN}_{\text{CH}_4} = \frac{[\text{H}_2]}{3[\text{CO}] + 4[\text{CO}_2]} = 1 \div 1.1,$$

$$\text{SN}_{\text{CH}_3\text{OH}} = \frac{[\text{H}_2] - [\text{CO}_2]}{[\text{CO}] + [\text{CO}_2]} = 1.5 \div 2.1,$$

where [H2], [CO] and [CO2] are, respectively, molar concentrations of the respective compound in the feedstock. For the case of methanol synthesis, a SNCH3OH of 2 refers to stoichiometric ratios, whereas values over and under 2, refer to over- and sub-stoichiometric ratios, respectively. For the case of methanation, a SNCH4 of 1 refers to a stoichiometric ratio of the reactants.

Renewable hydrogen is required to ensure clean POGs valorization. In the investigations reported in [25], three possible hydrogen production processes from renewables were considered: Proton Exchange Membrane electrolysis (PEM), Solid Oxide Electrolysis Cell (SOEC) and biomass gasification. Considering the high amount of expected required hydrogen for enriching the steelworks off-gases, biomass process appears not suitable and not mature yet, while PEM and SOEC electrolyzers show the following advantages:

- PEM is more stable in case of fluctuations of power supply as in the case of green power, and the process is carried out at low temperatures with low issues related to equipment choice and corrosion;
- SOEC is attractive if high temperature heat source is available and/or a considerable amount of industrial waste heat can be recovered.

Starting from these premises, different case studies were simulated:

- 3 related to the production of methane
- 1 related to the production of methanol
- 1 related to the combined production of methane and methanol
Table 3. Main results of preliminary simulated case studies.

<table>
<thead>
<tr>
<th>ID</th>
<th>Product</th>
<th>Description</th>
<th>Main outcomes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₄</td>
<td>100% utilization of the available POGs to produce methane</td>
<td>Largest hydrogen and consequently electrolysis requirement (between about 2 and 4 GW)</td>
</tr>
<tr>
<td>2</td>
<td>CH₄</td>
<td>Methanation of POGs that are currently used in the power plant</td>
<td>Almost complete carbon and H₂ conversion</td>
</tr>
<tr>
<td>3</td>
<td>CH₄</td>
<td>Methanation of specific amounts of the POGs in order to replace the NG demands of the plant</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>CH₃OH</td>
<td>Methanol synthesis of POGs that are currently used in the power plant</td>
<td>Reusing the residual hydrogen and/or optimum hydrogen utilization during methanol synthesis can significantly reduce the associated electrolysis demands</td>
</tr>
<tr>
<td>5</td>
<td>CH₄ + CH₃OH</td>
<td>Methanation of specific amounts of the POGs in order to replace the NG demands of the plant and for the production of significant quantities of methanol</td>
<td></td>
</tr>
</tbody>
</table>
Details of the investigations are provided in [23], however the main results are summarized in Table 3.

3 Reactors and dispatch controller

Laboratory and pilot scale test campaigns were carried out for three syntheses reactors (i.e., two for methane and one for methanol productions) in stationary and dynamic conditions and using synthetic and real off-gases [26].

The final developed methane production reactors were respectively an additively manufactured structured fixed-bed reactor (Fig. 2a) by Chair of Energy Process Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg [27,28] (REAC1) and a reactor setup using wash-coated honeycomb monoliths as catalyst (Fig. 2b) by Chair of Process Technology and Industrial Environmental Protection, Montanuniversität Leoben [29] (REAC2). A new multi-stage methanol reactor concept was designed, commissioned and extensively tested at pilot-scale (Fig. 2c) by Air Liquide [30] (REAC3).

To ensure the optimal management of the synthesis reactors operation when implemented in steelworks, a dispatch controller was developed and tested [31].

More details about both reactors and controller are provided in the next subsections.

3.1 Additively manufactured structured fixed-bed reactor for methane synthesis – REAC1

The final design of REAC1 was obtained starting from a structured fixed-bed reactor concept for catalytic methanation using heat pipes for removing heat from the reaction zone and the reactor in general [32]. In particular, this first version of the reactor is constituted by a block of stainless steel with 9 reaction channels filled with Ni/Al₂O₃ catalyst pellets; internal pre-heating and heat pipe cooling are provided. Two stages are ensured by the reactor with intermediate water sequestration. A gas analyzer makes it possible to know the composition of outlet stream. Dynamic trials were carried out by using BFG with up to ± 20% in syngas power, SNCH₄ equal to 1.04 and a reactor pressure of 4 bar. The main outcomes of the trials are [33]:

- full methane yield after two-stage;
- no influence of cycle time on the methane yield and hydrogen conversion;
- no increase in catalyst deactivation through dynamic operation caused and same gas quality as in steady-state operation;
- shift of conversion from 1st to 2nd stage by increasing syngas power, probably due to kinetic limitation in the second half of the reactor.

Considering these results, an innovative, additively manufactured reactor concept was designed to overcome kinetic limitation in the second half of the reactor by increasing residence time towards outlet and to improve kinetics by higher temperatures [34]. The reactor has a highly intensified concept, being very compact with a specific mass of 0.36 kg/kW and with 52% of functional volume. Its core is a conic reaction channel, with a lattice structure for feed gas preheating and of heat pipes for efficient heat removal. Its concept makes it scalable by increasing the number of the core elements. A bench-scale reactor prototype, namely ADDmeth1 (Fig. 2a), was implemented; methanation of BFG and BOFG was
successfully demonstrated achieving respectively 93.5% and 95.0% methane yields in single-stage process [35]. Kinetic and equilibrium limitations were observed respectively for BFG and BOFG. The reactor showed desired effect of temperature stabilization but also an increased sensitivity to the input variables (e.g., changes of the inlet volume flow rate highly affect cooling and gas inlet temperatures).

3.2 Methane production through a reactor setup using wash-coated honeycomb monoliths as catalyst – REAC2

The second methane production reactor consists of a flexible reactor concept with honeycomb catalyst, modular and simple to scale-up, holding enhanced stand-by properties and pressure losses. Such honeycomb catalyst (Fig. 3) holds a cordierite structure with high thermal shock resistance; it is two-stage wash-coated with Boehmite and Nickel that constitute the active material. Honeycombs are arranged in compartments allowing cyclic operation enhancing load flexibility; in addition, besides catalyst action, the ceramic carrier enables heat storage.

A laboratory scale reactor (Fig. 2b) was setup including 3 reactors in series and having the following maximum operating parameters:

- maximum pressure of 20 bar;
- maximum temperature of 700 °C;
- maximum flowrate of 50 NL/min.

Stationary and dynamic experimentations have been carried out using both synthetic BFG and BOFG and bottled real gases [29]. In case of dynamic trials [36], the dynamic parameters and operating modes are schematically reported in Figure 4. In particular, they refer to the following transient changes of:

- total volume flow in the form of gas hourly space velocity;
- gaseous feedstock composition;
- operating conditions in terms of pressure and temperature;
- hydrogen amount to reach suitable SNCH4.

In addition, the possibility has been considered of having a recirculation stream.

During steady-state experiments, full COx conversion was obtained with a hydrogen surplus of 4%. In case of bottled real gases additional gas cleaning was required (e.g., with CuO-coated activated carbon adsorbents). Only small variation in COx conversion and dry product gas composition was observed in dynamic experiments for load changes of ±25% in syngas power in the range of minutes and hours. Obtained results and performance for honeycomb catalyst were repeatable and consistent in long-term trials.

3.3 Multi-stage reactor for methanol synthesis – REAC3

A multi-stage reactor was basic designed including the analytical concept for producing methanol from unconventional syngas as POGs from steel plants. The new multi-stage
pilot plant (Fig. 2c) includes inter-stage condensation and separation; it allows up to 20 kg/h of methanol production. It was tested for more than 2300 hours of operation to validate this new generation of CO$_2$ to CH$_3$OH reactor concept. Very effective conversion rates (i.e., near to 100% for CO and slightly lower for CO$_2$) were obtained under once-through conditions (meaning without recycling) by using unconventional feedstock rich in nitrogen like the steelworks POGs. The once-through operation allows reacting very quickly to fluctuation towards feed compositions as well as changes in the load. In addition, even with fluctuating amount of feed, high CO concentration, high maximum temperature, the amount of by products are still lower than 5000 wt. ppm, as shown in Table 4. Consequently, proper distillation of raw methanol is feasible even in fluctuating conditions.

### 3.4 Dispatch controller for optimal management of syntheses reactors with POGs

A dispatch controller was developed to ensure safe operation of the synthesis reactors and efficient distribution of the POGs between internal steelworks users, power plant and synthesis reactors by simultaneously addressing dynamic constraints of steelworks, reactors and electricity grid services (strictly linked with green hydrogen production).
It was developed based on the Economic Hybrid Model Predictive Control (EHMPC) approach [31]; the controller concept is depicted in Figure 5.

The controller integrates a set of process and forecasting models based on physical/chemical principles and machine learning [37], implements a Mixed Integer Linear Programming (MILP) approach and includes a set of constraints related to the limit ranges of the operating conditions of each involved equipment/process unit (Tab. 5).

The controller objective function minimizes both economic and environmental impact in terms of CO2 emissions:

$$
\min_t \sum_{k=0}^{t+N_p} \left[ J_{H_2}(k) - J_{revenues}(k) + J_{CO_2}(k) + J_{OPEX}(k) + C_F(k) \right],
$$

(3)

where $J_{H_2}(k)$ are costs related to PEM electric energy consumption (from low-cost renewable energy sources), $J_{revenues}(k)$ are revenues related to internal electricity generation, sale of methane and methanol, $J_{CO_2}(k)$ are costs related to environmental impact in terms of CO2 emissions for POGs usage in the power plant and burned in the torches, $J_{OPEX}(k)$ are operative costs related to the switching of PEM, reactors and power plant, and finally $C_F(k)$ are fictitious costs related to soft constraints, penalization on the gasholder level and penalization on the variation of volume flows.

DC was extensively tested through offline simulation and an online test campaign coupled to syntheses reactors.

One of the main results of the offline simulations was demonstrating that the feasibility of i3upgrade solutions strictly depends on hydrogen cost [9], confirming what already evident from the early i3upgrade stages with the conducted flowsheet simulations (see Section 2) [23].

Online tests of open loop architecture were done with the controller closing the loop through the models. The controller sent the control strategy to a server where a TANI server (OPC UA) application. Then the controller closing the loop through the models. The controller sent the control strategy to a server where a TANI server (OPC UA) application.

Four days test were performed for a total of 18 hours: each day two reactors are controlled in parallel through DC strategy. Online tests proved that the DC is suitable to obtain sufficiently smooth control strategies in real time with a temporal resolution of 1 minute and a forecasting horizon of 2 hours. Safe and flexible operations and high conversion rates were obtained during the dispatch-controlled operations of all the three i3upgrade reactors [38]. In particular, for REAC1, full methane yield was obtained after a two-stage methanation with intermediate water separation; for REAC2, high CO2 conversion rates of over 99% on average were reached; for REAC3, CO and CO2 conversions were over 99% and between 70-78% respectively.

4 Overview of the techno-economic analysis

Final investigations concerned techno-economic, costs and business case analyses for facilitating the implementation of i3upgrade solutions in the steelworks. It is important to highlight that prices developments were carried out following references as reported in the following list:

- Electricity price [39]
- Electricity price high [40]
- Electricity price volatility [41]
- MeOH prices (low + high) [42]
- NG price low [43]
- NG price high [44]
- 6.15 CO2 price (low + high) [43]

An agent-based model was developed [45] for medium/long term techno-economic scenario investigations/optimization. The behavior of each agent was modelled through a combination of system-dynamics and state charts, which are suited for describing event- and time-driven behaviors. The buyer/seller agent takes into account production/consumption constraints and OPEX/CAPEX, and revenues.

Three potential business cases were investigated for the implementation of hydrogen intensified syntheses in the steel industry:

- CASE A, single production of methane
- CASE B, single production of methanol
- CASE C, combined production of methane and methanol.

The business cases were analyzed considering the methane production for covering natural gas steel plant-internal demand and methanol sale to the market.

Since capital and operational costs (CAPEX and OPEX) are fundamental pillars to draw a draft business- and exploitation plan for hydrogen-intensified synthesis in integrated steelworks, for each business case, a detailed economic analysis has been carried out including the syntheses steps, the pipeline and the units for gas transport, cleaning and compression and the hydrogen production as last. The main results are reported in Figure 6. For CASE A, as reported in related part of Figure 6, 100% of the product energetic content refers to methane, and about 79% of total production costs belongs to the OPEX while the remaining to CAPEX. In particular, for CAPEX, the contributing component are the following sorted in descending order: electrolyzers (18% of the total production costs), methanation equipment (i.e., reactors, heat exchangers, flash drum) (1.6% of total production costs), compression units (1% of total production costs) and pipelines, gas cleaning, heat-related equipment, oxygen storage (0.4% of total production costs). While for OPEX, the most contributing components is electricity with 73.6% of total production costs followed by utilities, labor, insurance, taxes, maintenance with 5.4% of the total production costs. Finally, an amount of about 10% of cost reductions can be observed, which is related to the sale of oxygen that is a by-product of the hydrogen production by electrolysis. For CASE B (see related part in Fig. 6), the product energetic content is constituted 100% by...
Fig. 6. Production cost breakdown and effect of electricity price and CAPEX and OPEX share for case A: single methane production, case B: methanol production and CASE C: combined production of methane and methanol.
methanol, and CAPEX and OPEX are respectively responsible of 23% and 77% of total production costs. Also in this case, electrolyser is the main CAPEX contribution (15% of total production costs), followed by methanol production units (3.1% of total production costs), compression equipment (2.6% of total production costs) and other minor CAPEX with 1.7% of total production costs. In addition, electricity is again the main component of OPEX with 72.6% of total production costs, followed by utilities and other minor OPEX with 4.4% of total production costs. Oxygen contributes to about 10% of production costs reduction. Finally, CASE C, whose results are reported in related part of Figure 6, is characterized by the following distribution of product energetic content: 51% for methanol and 49% for methane. CAPEX and OPEX contribute respectively to 22.5% and 77.5% of total production costs. Electrolysis is again the main CAPEX responsible with 16.2% of total production costs and it is followed by methanol synthesis units (2.8% of total production costs), compression equipment (2.1% of total production costs) and methanation units (0.7% of total production costs). Electricity is again predominant in OPEX with 72.6% of total production costs; further minor OPEX contributes to 4.9% of total production costs. Then, about 9% of production costs reduction is achieved by selling oxygen. In all the three analyzed cases, electricity costs and volatility affect methane and methanol production: a cheap electricity price (i.e., 10-30 €/MWh) can lower the price of the two products to competitive levels while higher electricity prices (i.e., 50-80 €/MWh) lead to significant increases in methane and methanol prices.

It was proved, once again, that a dedicated low-cost hydrogen market is needed. Considering that hydrogen production and handling is responsible for over 80% of the total costs, low electrolyser costs, low electricity prices and highly efficient hydrogen production processes are fundamental to establish the i3upgrade solutions [46].

Three potential economic scenarios were then considered as depicted in Figure 7. In the first scenario, almost linear price increases for methanol, NG and CO2 are considered; an increase of electricity price is assumed in the period of the expected shutdown of conventional energy generation (between 2030 and 2038) followed then by a decrease of price. The second scenario is characterized by almost
constant methanol price, linear increase of NG and CO₂ prices and low electricity prices due to strong increase in renewables compensating for conventional systems shutdown. The final combined scenario includes low electricity price trend assuming significant support for expansion of renewable energies, and sharp rise of NG, CO₂ and methanol prices.

The third economic scenario shows the best prospects for a profitable operation of the three considered business cases. Figure 8 shows the Return Of Investment (ROI) for the three business cases calculated according to the third economic scenario. ROI equation is as follows:

\[
ROI = \frac{Profit}{Initial\ Investment}.
\]  

ROI>0 means profitability, and both three business cases are profitable only from 2040 onwards for the specific conditions of the third economic scenario as depicted in Figure 8.

Therefore, a sensitivity analysis has been carried out to study under which conditions the production of methane and/or methanol via POGs valorization could be a profitable business case. The ROI was computed based on electricity price (variation from 0 to 150 €/MWh), as this is one of the factors mostly affecting final production costs. NG, CO₂ and methanol prices for 2030 are considered constant, and their values are reported in Table 6. The year 2030 was chosen because EU should reduce its emissions by at least 55% that means that a significant drop on the current greenhouse gas emission levels is required soon. In addition, in ROI computation, maintenance was assumed to be 2% of total invest per year, 1.5% of total invest was included for insurance, administration, etc.. Furthermore, lifetime was included to deprecate all expenses.

The ROI including annuities and interests for 2030 and depending on the electricity prices is depicted in Figure 9 for the third economic scenario. The figure highlights the break-even electricity prices for a profitable operation:

- **CASE A** (Methane), electricity price < 15 €/MWh
- **CASE B** (Methanol), electricity price < 32 €/MWh
- **CASE C** (Methane & Methanol), electricity price < 26 €/MWh

CO₂ reduction potential was calculated considering the reference i³ upgrade steel mill for the three operational case reactors and by using the following CO₂ factors:

- \(64.5\ \text{kg}_{\text{CO₂}}/\text{MWh}_{\text{SNG}}\)
- \(0.1388\ \text{t}_{\text{CO₂}}/\text{MWh}_{\text{CH₃OH}}\)

### Table 6. Fixed prices for 2030 in third economic scenario.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit of measurement</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG</td>
<td>€/MWh</td>
<td>53.49</td>
</tr>
<tr>
<td>CO₂</td>
<td>€/t</td>
<td>74.50</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>€/MWh</td>
<td>107.32</td>
</tr>
</tbody>
</table>

Fig. 8. ROI for the single production of methane, the single production of methanol and the combined production of methane and methanol between the year 2020 and 2045 according to the third economic scenario.

Fig. 9. ROI accounting profit for 2030 in dependence of electricity prices.
No free allowances accounting to the EU-ETS Emission Trading System are considered in the calculation. The CO₂ emitted is directly linked to the amount of produced methane and methanol, thus, to achieve the highest possible savings, the reactors must operate at their maximum capacity.

Figure 10 shows the CO₂ savings adapted to the third economic scenario. Maximum CO₂ savings by 2030 are linked to the combined production of methane and methanol, followed by the single production of methanol. Scarce full load hours for the methanation reaction are considered between 2022 and 2034 due to expensive electricity and cheap NG. By 2050, the combined production of methanol and methane has still the highest CO₂ reduction potential, followed this time by the single production of methane.

Finally, production costs in energetic terms (€/GJ) for the three business cases in case of different electricity prices were compared to the NG and methanol market prices in 2021 [47,48] (see Fig. 11).

Single production of methane requires lower expenses independently of the electricity prices. On the other hand, single production of methanol shows the highest production costs due to lower carbon conversion, higher hydrogen
demand and higher feed compression costs. However, by comparing production costs with market prices for methane and methanol, the most profitable case appears single production of methanol, due to a break-even point at an electricity price lower than 30 €/MWh compared to about 10 €/MWh in case of single methane production.

5 Conclusions

The paper provides an overview of the main outcomes of a European project targeting chemical valorization of steelworks POGs through innovative reactors and advanced control system to produce methane and methanol. It was demonstrated that POGs can be chemically valorized if enriched by H₂ and, if suitable, additionally conditioned to remove trace compounds that can poison reactors catalysts. Simulations demonstrate advantages and disadvantages of different renewable hydrogen production processes and fundamental role of hydrogen in different POGs valorization scenarios. Three cutting-edge syntheses reactors have been designed, built and tested to obtain high CO₂ conversion rates and methane and methanol yields also in transient regimes, with a significant progress beyond the state of the art. A dispatch controller provides smooth control strategies in real time and safe and flexible operations of the three reactors by managing the right distribution and usage of steelworks POGs considering both standard energetic and novel chemical valorization, market prices and hydrogen production and availability. Cost, business case and techno-economic analyses demonstrate that industrial implementation of the investigated solutions can lead to significant environmental and economic benefits for steelworks, especially in the case of higher availability of green electricity and lower price of renewable energy sources compared to the current situation.

The results of i³upgrade contribute to the steelmaking sector decarbonization and pave the way to transfer and replicate the investigated solutions to other industrial sectors emitting significant amount of carbon-rich gases, by facilitating impact decrease and achievement of EU Green Deal objectives.

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